

Titre: Modélisation cinétique de la réduction de minerais par le monoxyde de carbone utilisés dans le procédé de combustion en boucle chimique
Title:

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Author:

Date: 2016

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Perreault, P. (2016). Modélisation cinétique de la réduction de minerais par le monoxyde de carbone utilisés dans le procédé de combustion en boucle chimique [Ph.D. thesis, École Polytechnique de Montréal]. PolyPublie.
Citation: <https://publications.polymtl.ca/2109/>

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Programme: Génie chimique
Program:

UNIVERSITÉ DE MONTRÉAL

MODÉLISATION CINÉTIQUE DE LA RÉDUCTION DE MINÉRAIS PAR LE
MONOXYDE DE CARBONE UTILISÉS DANS LE PROCÉDÉ DE COMBUSTION EN
BOUCLE CHIMIQUE

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THÈSE PRÉSENTÉE EN VUE DE L'OBTENTION
DU DIPLÔME DE PHILOSOPHIÆ DOCTOR
(GÉNIE CHIMIQUE)
AVRIL 2016

UNIVERSITÉ DE MONTRÉAL

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

Cette thèse intitulée :

MODÉLISATION CINÉTIQUE DE LA RÉDUCTION DE MINÉRAIS PAR LE
MONOXYDE DE CARBONE UTILISÉS DANS LE PROCÉDÉ DE COMBUSTION EN
BOUCLE CHIMIQUE

présentée par : PERREAULT Patrice

en vue de l'obtention du diplôme de : Philosophiæ Doctor

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DÉDICACE

À Marisol, Mateo, Nathan, Lea et tous les autres à venir . . .

REMERCIEMENTS

Mes sincères et amicales remerciements à Sébastien Riffart (Total), sans qui ce projet ne serait demeuré qu'un projet de recherche de quelques mois. Grâce à sa vision des retombées potentielles des résultats préliminaires de ce premier projet de recherche, une maîtrise, un brevet et une thèse sont nés. Je remercie également et sincèrement Hélène Stainton et Mahdi Yazdapanah de chez Total avec qui j'ai eu des échanges très constructifs.

Merci à mes collègues, en particulier à François-Xavier Chiron, qui a su m'amener à des niveaux supérieurs en pointant mes lacunes et possibilités. Au plaisir de te croiser dans une conférence et d'en boire quelques-unes à ta santé.

Merci au professeur émérite Michel Soustelle, de l'École nationale supérieure des mines de Saint-Étienne, avec qui j'ai échangé et qui m'a grandement éclairé sur les voies de modélisation des réactions gaz-solide en tenant compte des caractéristiques des solides réels.

Je tiens à remercier les professeurs du département de Génie chimique, en particulier au chargé d'enseignement Patrice Farand, pour les nombreuses possibilités d'enseignement, ainsi que Jamal Chaouki et Robert Legros pour m'avoir montré de la considération. Merci aussi aux techniciens, en particulier Jean Huard qui doit se réveiller en sursaut la nuit en m'entendant lui demander des raccords Swagelok...

Je ne peux également passer sous silence la grande source d'inspiration que représente Marisol López Vera, ma femme. Elle a entièrement appuyé mon retour aux études après quelques années de travail en industrie, malgré la baisse de salaire qui en résultait. C'est elle qui a tenu le fort familial durant certaines soirées et fins de semaine d'expérimentation et de rédaction de thèse. Elle a aussi été le ciment familial et de couple. Je te remercie du fond de mon cœur. Merci aussi à Mateo, mon grand de 6 ans, une source d'inspiration : je me souviendrai toute ma vie de cette fois où tu t'es assis devant mon ordi en me disant que tu travaillais sur ton doctorat ! Merci aussi à Nathan, mon bébé naissant, qui me permet de réfléchir à des questions complexes de modélisation en ne dormant pas la nuit ! Merci ma petite famille.

Merci également à Miles Davis, John Coltrane, Lila Downs, Conchita Buika, Bernard Adamus, René Aubry et Tom Waits (entre autres) de m'avoir accompagné durant le long travail de traitement de données, de modélisation et de rédaction.

Finalement, je tiens à remercier Gregory-S. Patience, mon directeur de thèse, sans qui je serais probablement encore un ingénieur non gradué oeuvrant à des tâches répétitives. Par

la grande liberté qu'il m'a accordée, il m'a permis de développer mon autonomie, mais aussi ma façon particulière d'envisager la modélisation cinétique (malgré tous nos désaccords). Il a toujours fait preuve d'une grande disponibilité (p. ex. réponses aux courriels en pleine nuit), et était toujours disponible pour me guider dans mes démarches ou pour tout simplement pour discuter. Merci Gregory.

RÉSUMÉ

Le procédé de combustion en boucle chimique est un procédé de production d'énergie générant un courant ne contenant que du dioxyde de carbone et de l'eau. Contrairement aux autres procédés de production d'énergie basés sur la combustion, les gaz ne sont pas dilués dans un courant riche en diazote (N_2). Pour séparer le CO_2 sans la pénalité énergétique de post-séparation, on utilise l'oxygène contenu dans un oxyde métallique (solide), séquentiellement oxydé et réduit dans deux réacteurs interconnectés. La configuration de lit fluidisé s'est graduellement imposée dans la littérature. Dans le réacteur d'oxydation, opéré en colonne montante (*riser*), le solide est réoxydé en présence d'air, et dans celui de réduction, opéré en régime bullant, on alimente un combustible (solide, liquide ou gazeux) qui servira d'agent réducteur. On récupère de l'énergie essentiellement dans le réacteur d'oxydation (variation d'enthalpie négative), mais certains oxydes sont aussi réduits par le biais d'une réaction exothermique (p. ex., cuivre). La somme des enthalpies d'oxydation et de réduction du solide est égale à la variation d'enthalpie de la combustion du combustible utilisé. Le déploiement du procédé à l'échelle industrielle repose sur l'identification d'un solide (porteur d'oxygène) pouvant transférer une grande quantité d'oxygène sur une base massique (capacité de transfert d'oxygène), ayant une cinétique rapide (minimisation du volume nécessaire pour une conversion donnée), résistant à l'attrition, non toxique, peu cher et chimiquement stable (désactivation lente). Les critères de non-toxicité et de faible coût favorisent l'utilisation de minerais dans le procédé (par opposition aux oxydes de synthèse).

Le dimensionnement du procédé repose sur la connaissance des cinétiques d'oxydation et de réduction du solide. Or, la réaction d'oxydation est toujours beaucoup plus rapide (quelques secondes) que sa réduction (quelques minutes). Ainsi, pour le dimensionnement, la détermination de la cinétique de réduction est suffisante. L'ilménite (de formule $FeTiO_3$) s'est graduellement imposée comme porteur d'oxygène d'origine minérale de référence en raison de son abondance et de sa tenue mécanique exemplaire. Malheureusement, celui-ci est sujet à l'agglomération et possède une capacité de transfert d'oxygène limitée. Nous avons préalablement identifié la pyrolusite (de formule MnO_2 dans sa forme fraîche) comme porteur d'oxygène potentiel de remplacement pour l'ilménite. La pyrolusite est un minerai amorphe de manganèse, beaucoup moins cher que l'ilménite et abondant. Lors de sa calcination, son degré de cristallinité augmente, et on peut identifier la bixbyite (Mn_2O_3), l'hausmannite (Mn_3O_4) et la manganosite (MnO) par analyse de diffraction à rayons X. Un des objectifs de cette thèse est d'identifier le meilleur candidat pour le procédé de combustion en boucle chimique en procédant à la comparaison des cinétiques de réduction par le monoxyde de

carbone (CO) de l'ilménite et de la pyrolusite.

L'ilménite a d'abord été préoxydé à 1000 °C durant 24 h afin de diminuer sa tendance à l'agglomération par frittage. Malheureusement, cette pratique a comme effet de diminuer sa capacité de transfert d'oxygène en raison de l'augmentation de sa cristallinité, et ce, malgré une augmentation de sa capacité de transfert d'oxygène théorique (formation de pseudobrookite ferrique, de formule Fe_2TiO_5). La capacité de transfert d'oxygène de l'ilménite fraîche est de 1,7 %, en comparaison à 1,2 % pour la pseudobrookite ferrique, lorsque réduite durant 2 min avec du monoxyde de carbone à 910 °C. Aux mêmes conditions, la pyrolusite transfère 2 %, et cette capacité double si on coalimente de l'hydrogène (sur la base de l'oxygène transféré au CO seulement, c.-à-d. en excluant la quantité d'hydrogène converti en eau).

La cinétique de réduction des deux minerais peut être caractérisée de la même façon : soit une réaction de surface entre les molécules de CO et l'oxygène de surface, et une réaction de réoxydation des sites réduits par l'oxygène en provenance du réseau cristallin. Le modèle permet d'expliquer plus de 90 et 95 % de la variance dans les données, pour l'ilménite et la pyrolusite, respectivement. Bien entendu, les valeurs numériques des énergies d'activation des deux oxydes diffèrent grandement. Dans le cas de la réaction de surface, elle est de 51 kJ mol^{-1} pour l'ilménite. Cette valeur est négative dans le cas de la réaction directe de réduction de la pyrolusite, en accord avec la diminution de l'avancement de cette réaction avec la température. La capacité de transfert d'oxygène tend vers une asymptote pour une augmentation de la température. Aussi, la réaction de réduction des sites surfaciques est réversible, c.-à-d. qu'il est possible de réduire le CO_2 en CO à une vitesse augmentant avec la température.

La caractérisation cinétique de la réduction de l'ilménite par le CO a aussi permis de déterminer que cette réaction est limitée par le transfert de matière externe, soit entre le volume du gaz et la surface de l'oxyde (théorique du film). Dans le cas de la pyrolusite, l'analyse des critères de Mears et de Weisz-Prater a permis de conclure que le régime est contrôlé par la cinétique. La réaction de réoxydation des sites surfaciques réduits par le CO présente une énergie d'activation de 89 kJ mol^{-1} pour l'ilménite, alors qu'elle est de 55 kJ mol^{-1} dans le cas de la pyrolusite. La réaction moins aisée de réoxydation de la surface dans le cas de l'ilménite peut être expliquée par sa structure cristalline : des couches alternées Ti et Fe, induisant une certaine résistance étant donné que l'oxygène lié au titane n'est pas impliqué dans la réaction de réduction. L'effet de la cinétique plus rapide de la réduction de la pyrolusite se reflète sur l'inventaire de solide nécessaire dans le réacteur de réduction : une diminution d'un ordre de grandeur par unité de puissance thermique. En considérant une cinétique moyenne, on trouve des valeurs de 4,3 et $0,41 \text{ t MW}^{-1}$ pour l'ilménite préoxydée et

la pyrolusite, respectivement.

Il a été question de modéliser la cinétique de ces réactions de réduction à l'aide de l'approche classique mécanistique. Le choix de cette méthode repose sur les nombreuses incongruités retrouvées dans la littérature concernant la cinétique de réduction de l'ilménite par le CO. Des auteurs différents (mais parfois les mêmes auteurs travaillant avec les mêmes données expérimentales) ont caractérisé la cinétique de réduction de l'ilménite par le CO tour à tour avec des modèles morphologiques (ne considérant que l'évolution de la structure du solide) à coeur rétrécissant (*shrinking core*) en une et trois dimensions (géométrie plane et sphérique, respectivement), avec des ordres de réaction variant entre 0,67 et 2 pour le gaz, et des énergies d'activation allant du simple au double, révélant du coup la nature de pur ajustement mathématique de cette approche de modélisation. Nous avons montré que presque la moitié des formes canoniques de ces modèles parvenait à caractériser la courbe de conversion du solide, d'où la nécessité d'un modèle plus rigoureux.

Malheureusement, la modélisation cinétique selon l'approche mécanistique fait intervenir des paramètres de surface difficilement mesurables. Par exemple, pour exprimer la variation de la concentration de sites oxydés, nous avons besoin de quantifier la densité surfacique de sites actifs (soit des atomes d'oxygène en surface). Nous avons réussi dans un premier temps à justifier la validité de notre approche ayant recours à un paramètre ajusté pour cette quantité. Les valeurs numériques ajustées ont permis de corroborer la diminution dans le temps de la densité surfacique de sites actifs avec le nombre de cycles de réduction. Ce phénomène peut être interprété par la tendance de l'ilménite à l'agglomération. Dans un deuxième temps, nous avons établi une méthode d'estimation de la densité surfacique de sites actifs. On peut interpréter la méthode comme une courbe de titration simulée. En effet, en discriminant entre réaction de surface et de diffusion, il est possible d'estimer la densité surfacique de sites en prenant l'aire sous la courbe de la concentration du pic initial de CO₂ formé dans le cas de la réduction par le CO. Nous en avons illustré le principe à l'aide de la cinétique de réduction de l'ilménite : une fois la surface complètement réduite, on observe que la concentration de CO₂ diminue jusqu'à zéro, n'étant affecté que par la dispersion axiale dans le réacteur et le transfert de matière.

L'hypothèse sous-jacente à la méthode proposée est la supériorité de la vitesse de la réaction surfacique par opposition à celle de diffusion. La méthode respecte également les critères des méthodes de mesures chimiques existantes, soit l'utilisation d'une sonde chimique identique ou similaire à celle du réactif, et des conditions expérimentales de caractérisation de la surface le plus près possibles des conditions où la réaction a lieu. La méthode nécessite par contre un certain comportement chimique afin de fournir une borne supérieure pour la densité

surfacique de sites, soit la saturation de la surface par les réactifs. Les profils de gaz obtenus lors de la réduction de la pyrolusite par le CO ont permis de constater une concentration maximale asymptotique de CO₂ produite pour des concentrations de CO croissant. Ce faisant, nous avons pu estimer la densité surfacique de sites actifs de la pyrolusite à 40 μmol m⁻², une valeur en accord avec les valeurs mesurées publiées d'oxydes de manganèse de synthèse.

Nous nous sommes aussi intéressés à des améliorations à apporter au procédé CLC, en particulier à la valorisation des gaz de combustion. Nous avons en effet démontré la possibilité du reformage de gaz de combustion en gaz de synthèse à l'aide de la pyrolusite réduite. En effet, nous avons montré que la pyrolusite soumise à une centaine de cycles d'oxydoréductions sous méthane et oxygène (séquentiellement) à 800 °C devenait apte à réduire le CO₂ en CO, de même que la vapeur d'eau en hydrogène. La production spécifique maximale de monoxyde de carbone atteint 5,5 mol kg⁻¹ entre 810 et 960 °C, même pour un temps de contact de seulement 0,01 s. Cette valeur correspond à 100 fois celle des meilleurs catalyseurs de synthèse, les pérovskites à base de Sr, Ce et Fe. De même, la production d'hydrogène a atteint un maximum de 4,8 mol kg⁻¹ à 947 °C, soit le double des valeurs obtenues à l'aide du cycle dit hercynite à l'aide de catalyseurs de CoFe₂O₄ et Al₂O₃.

Finalement, nous nous sommes intéressés au couplage d'un oxyde de cuivre et d'un oxyde de calcium dans un contexte de production d'hydrogène. Pour pallier les inefficacités du procédé classique d'enlèvement du CO₂ des gaz de reformage dans une tour de lavage, nous avons fait appel à un oxyde mixte cuivre-calcium. Cet oxyde mixte, combinant les propriétés du procédé CLC et les cycles à carbonate, permet d'éviter le recours à de l'oxygène pur pour la régénération de l'oxyde de calcium. Dans cette configuration, la chaleur émise lors de la réduction d'un oxyde métallique fournit la chaleur de régénération de l'oxyde de calcium. CanMET nous a fourni un solide de synthèse combinant un oxyde de cuivre et de calcium, additionné d'un agent liant à base de ciment pour une résistance améliorée à la désactivation et à l'attrition. Cet oxyde mixte peut convertir jusqu'à 4,3 % en masse de CO₂ par masse initiale en carbonate sur la plage de température allant de 425 à 665 °C sous des concentrations de CO₂ entre 10 et 20 %. Nous avons également caractérisé sa cinétique de carbonatation à l'aide d'un modèle empirique de premier ordre à l'équilibre avec des énergies d'activation de 220 et 120 kJ mol⁻¹ avec un coefficient de corrélation d'au moins 99 %. De même, à l'aide de mesures répétées de surface spécifique BET avant et après les 15 premiers cycles de carbonatation-régénération, nous avons pu modéliser sa désactivation par frittage à l'aide d'un modèle de puissance d'ordre 0,5 et d'une constante de détérioration de 2,86 min⁻¹.

ABSTRACT

Secondary ilmenite (FeTiO_3) is an inexpensive mineral that became the most cited potential replacement oxygen carrier for the chemical looping process to the synthetic expensive and toxic nickel oxide. Ilmenite has excellent mechanical stability, adequate heat capacity to transfer heat from the air reactor to the fuel reactor, but possesses a modest oxygen transfer capacity and is prone to agglomeration. One way to minimize its sintering tendency is to preoxidize the mineral, producing ferric pseudobrookite (Fe_2TiO_5) with an increased theoretical oxygen transfer capacity. However, fresh ilmenite has a higher oxygen transfer capacity, possibly due to the increased crystallinity of the preoxidized form. Ilmenite can transfer up to 1,7 %, i.e. higher than that of ferric pseudobrookite (1,2 %), when reduced for 2 min with carbon monoxide (CO) at 910 °C. Unfortunately, fresh ilmenite cannot be used in the chemical looping process (CLC) due to the high sintering risks.

We compared the oxygen transfer capacity of pyrolusite as a potential replacement oxygen carrier for ilmenite. Pyrolusite is an amorphous inexpensive and nontoxic manganese ore, that can transfer almost than double the oxygen (2 % when reduced with CO for 2 min) without any agglomeration risks. We compared the kinetics of preoxidized ilmenite to that of pyrolusite, by deriving mechanistic kinetic models. For both oxides, the model assumes that CO reacts with surface oxygen atoms, and that bulk oxygen replenishes the surface oxygen. The model explains more than 90 and 95 % of the variance of the data, for ilmenite and pyrolusite, respectively. However, the associated activation energies differ greatly. The activation energy for the surface reaction between CO and ilmenite reaches 51 kJ mol^{-1} . However, the value of the kinetic constant for the direct CO reduction of pyrolusite decreased with temperature (negative activation energy), as expected: The oxygen transfer capacity reached an asymptote with increasing temperature. In addition, the reaction between ilmenite and CO is limited by external mass transfer between the bulk gas phase and the surface, while the surface reaction governs the reduction of pyrolusite. The elementary step describing the reoxidation of the surface sites with oxygen from the lattice has an 89 and 55 kJ mol^{-1} activation energy for ilmenite and pyrolusite, respectively. The fastest kinetics of the reduction of pyrolusite with CO has a significant effect on the solid inventory needed in the fuel reactor of the CLC process: a commercial CLC process with pyrolusite would require 10 times less solids than one with ilmenite.

By modeling the reduction kinetics following a mechanistic approach, the surface site density of active sites (oxygen atoms in a surface position) had to be characterized. We estimated this

surface parameters two approaches: as a curve fitting parameters, and by calculating the area under the CO_2 concentration curves for a saturated surface reaction. The two approaches have proven valid: The fitted value illustrated the agglomeration tendency of ilmenite, and the indirect measurement method (simulated gas-solid titration curve) revealed the saturated nature of the surface reaction (asymptote at $40 \mu\text{mol m}^{-2}$). Both methods yielded numerical values in agreement with that reported measurements for synthetic bulk oxides.

We also investigated potential improvements to the chemical looping process. In its current form, the process generates a pure CO_2 stream after condensation of water. When sequestering CO_2 in geological medium, the risk of fracturing and further upward CO_2 migration and possible escape is never completely avoided. A better solution might be to convert the gas phase CO_2 in solid calcium carbonate in a combined CLC and calcium cycle (CaL). However, regeneration of calcium oxides requires pure O_2 to avoid generated diluted CO_2 in nitrogen, which would only displaced the problem of CO_2 separation. Combining CLC with CaL allows for a definitive solution: the heat produced during the reduction of a metal oxide (e.g. copper) provides the heat for the CO_2 sorbent regeneration. Finding a suitable synthetic solid combining attrition and deactivation resistant combined CO_2 sorbent and chemical looping agent is crucial. CanMET provided us with a homogeneous calcium copper oxide containing a cement binder for that purpose. We characterized its deactivation and carbonation kinetics during the first 15 carbonation-calcination cycles between 425°C to 665°C (calcination at a maximum 900°C temperature). The sorbent can convert up to 4,5 % of its mass in calcium carbonate, following an equilibrium carbonation kinetics with activation energies of 220 and 120 kJ mol^{-1} for the forward and reverse reaction, respectively. We also showed that a gradual increase in crystallinity with time on stream decreased the reaction rate. We modeled this phenomenon and were able to increase the fit to account from 97 % to 99 % of the variance in the data. We use the generalized power law model with a 0.5 order and $2,86 \text{ min}^{-1}$ to model the deactivation of the sorbent by sintering.

A final improvement to the CLC process is to reform combustion gases into a mixture of CO and H_2 , by taking advantage of the CO_2 reduction and water splitting properties of aged pyrolusite. Specific CO production is 10–100 times higher than Sr, Ce, and Fe doped perovskites and $\text{Y}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ perovskites, the best published material for CO_2 reduction. At a contact time of 0,01 s and at temperatures ranging from 810 – 960°C the maximum specific CO production was $5,5 \text{ mol kg}^{-1}$. A combined kinetic-axial dispersion hydrodynamic model accounts for 97 % of the variance in the data assuming the reaction rate is first order in CO_2 and surface reduced sites and in equilibrium with the reverse reaction—a first-order reaction in CO with surface oxidized sites. A second reaction accounts for the diffusion of surface oxygen to the bulk lattice. Hydrogen productivity peaked at $4,8 \text{ mol kg}^{-1}$ at 947°C ,

which is twice as high as reported in previous studies on CoFe_2O_4 and Al_2O_3 in the hercynite cycle.

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LISTE DES SIGLES ET ABRÉVIATIONS

k_B	Constante de Boltzmann ($1,381 \times 10^{-23} \text{ J K}^{-1}$)
k_c	Coefficient de transfert de matière ($\text{kg m}^{-2} \text{ s}^{-1}$)
k_i	Constante cinétique d'une réaction i (unités selon l'ordre et la nature de la réaction)
k'_i	Constante cinétique d'une réaction de surface i (unités selon l'ordre et la nature de la réaction)
m_{molec}	Masse d'une molécule adsorbée molecule (g)
n	Nombre de sites vacants (sans dimension)
r_i	Vitesse d'une réaction i ($\text{mol m}^{-3} \text{ s}^{-1}$)
t	Temps (s)
u_z	Vitesse superficielle d'un gaz (m s^{-1})
y_i	Fraction molaire d'une espèce i (sans dimension)
z	Hauteur (m)
C_i	Concentration d'une espèce i (mol m^{-3})
$C_{i,b}$	Concentration d'une espèce i dans le volume (mol m^{-3})
$C_{i,s}$	Concentration à la surface d'une espèce i (mol m^{-3})
D_e	Diffusivité effective ($\text{m}^2 \text{ s}^{-1}$)
D_z	Coefficient de dispersion axiale ($\text{m}^2 \text{ s}^{-1}$)
E_a	Énergie d'activation (kJ mol^{-1})
F	Flux de molécules incidentes ($\text{m}^{-2} \text{ s}^{-1}$)
K_i	Constante d'équilibre d'une réaction i (unités selon l'ordre et la nature de la réaction)
M_i	Masse molaire d'une espèce i (g mol^{-1})
N	Nombre total de sites de surface (sans dimension)
N_{Av}	Nombre d'Avogadro ($6,022 \times 10^{23} \text{ mol}^{-1}$)
N_{CO*}	Densité surfacique de molécules de CO adsorbées (mol m^{-2})
N_r	Concentration initiale d'atomes d'oxygène dans le lit réactionnel (mol m^{-3})
N_s	Densité surfacique de site (mol m^{-2})
P	Pression (Pa)
Q_i	Chaleur dégagée ou absorbée lors d'une réaction i (kJ mol^{-1})
R	Constante des gaz parfaits ($8,314 \text{ J mol}^{-1} \text{ K}$)
R_O	Capacité de transfert d'oxygène (massique)

$R_{O,th}$	Capacité de transfert d'oxygène théorique (massique)
R_p	Rayon d'une particule (m)
S	Probabilité de collage d'une molécule lors d'une collision avec une surface
SS_{BET}	Surface spécifique BET ($\text{m}^2 \text{g}^{-1}$)
T	Température (K)
V_i	Lacune d'une espèce i
$\dot{V}$	Débit volumique ($\text{m}^3 \text{s}^{-1}$)
X	Conversion (sans dimension)
α	Conversion d'un solide (sans dimension)
ϵ	Porosité d'un lit de particules (sans dimension)
γ_i	Concentration normalisée d'une espèce i (sans dimension)
ρ_b	Masse volumique vrac d'un lit de particules (kg m^{-3})
ρ_p	Masse volumique des particules (kg m^{-3})
θ_i	Degré de recouvrement d'une espèce i (sans unités)
ΔE_f	Énergie de formation d'un défaut ponctuel (kJ mol^{-1})
ΔH	Variation d'enthalpie (kJ mol^{-1})

CHAPITRE 1 INTRODUCTION

Malgré des consommations d'énergie à la baisse pour les pays membres de l'Organisation de coopération et de développement économiques (OCDE), les besoins mondiaux en énergie ont continué de croître en 2015 (+0,9 % d'augmentation en 2014 [1]), et une augmentation de 30 % est à prévoir d'ici 2040, essentiellement pour combler les besoins de l'Inde, la Chine, l'Afrique, le Moyen-Orient et l'Asie du Sud-Est [2]. Le pétrole demeure le combustible le plus utilisé (32 %, suivi par le charbon (30 %) et le gaz naturel (22 %)), tout en continuant de perdre des parts de marchés depuis les 15 dernières années [1, 3]. Conséquemment, les émissions de Gaz à effet de serre (GES) ont également continué d'augmenter, atteignant 32 190 Mt de dioxyde de carbone (CO_2) équivalent [3]. Les 30 dernières années ont été les plus chaudes qu'ait connues l'hémisphère nord depuis 1400 ans et les gaz à effet de serre d'origine anthropomorphiques en sont les grands responsables [4]. Les moyens de décarboniser la production d'énergie sont multiples et les technologies de captation du CO_2 sont celles présentant un potentiel immédiat, même doit si leur déploiement doit être accéléré [5].

On distingue les solutions de captation de CO_2 pré- et postcombustion, soit celles intervenant en amont ou en aval de l'étape de combustion. La technologie de postcombustion la plus mature est l'absorption du CO_2 à l'aide de solvant. Or, en plus du coût en capital élevé (applicable de fait à l'ensemble des technologies de captation), la technologie d'absorption présente plusieurs barrières à son déploiement commercial : parmi celles-ci, une pénalité énergétique de 12 à 16 % pour la régénération du solvant [6, 7], de même que sa dégradation par le dioxyde de soufre (SO_2), l'oxygène (O_2), et les oxydes d'azote (regroupés sous la formule générique NO_x) présents dans les gaz de combustion [8]. L'oxycombustion, tout comme la CLC, sont des technologies de précombustion permettant de générer des gaz de combustion ne contenant que du CO_2 et de l'eau, en ayant recours à de l'oxygène pur (O_2) au lieu d'air (majoritairement constitué d'azote). Or, alors que pour l'oxycombustion, la combustion survient en présence d'oxygène pur en phase gazeuse, la source d'oxygène dans la CLC est solide : un oxyde métallique est séquentiellement oxydé et réduit à haute température (700 à 1000 °C). La différence est de taille : la production d'oxygène pur par distillation cryogénique rend le procédé d'oxycombustion non compétitif d'un point de vue économique en raison d'une pénalité énergétique de 20 à 35 % [6, 9].

Malgré cet avantage de la CLC, plusieurs défis demeurent pour son déploiement commercial. La compétitivité économique du procédé CLC repose sur les coûts des émissions de GES dans des cadres réglementaires comme le protocole de Kyoto ou encore la bourse naissante

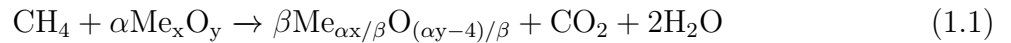
du carbone. D'un point de vue technique, bien que plusieurs incertitudes techniques aient été levées, la cinétique de réduction et d'oxydation des porteurs d'oxygène le plus intéressants demeure à caractériser. En effet, nous verrons aussi que la faisabilité autant économique que technique repose sur l'utilisation de porteurs d'oxygène abondants, peu chers, résistants à l'attrition, et non toxiques. Plusieurs oxydes métalliques d'origine minérale répondent à ces critères, mais leur cinétique de réduction est soit inconnue, soit contradictoire sur la base des travaux de recherches publiés.

1.1 Définitions et concepts de base

1.1.1 Combustion en boucle chimique

La CLC est un procédé de production d'énergie ne générant que du CO_2 et de la vapeur d'eau. Le procédé CLC peut ainsi être considéré comme un procédé d'oxycombustion sans les importants coûts de séparation de l'oxygène contenu dans l'air. Ainsi, on peut concentrer le CO_2 obtenu par simple condensation de l'eau et par exemple, comprimer et séquestrer le CO_2 dans le sous-sol géologique. L'intérêt et la justification économiques de ce procédé résident dans l'évitement d'émissions de GES, c.-à-d. au niveau des coûts évités de ces émissions dans un cadre réglementaire (par exemple, le protocole de Kyoto).

La stratégie de mise en oeuvre du procédé consiste à séquentiellement oxyder et réduire un oxyde métallique en faisant circuler ce dernier dans deux réacteurs interconnectés : l'oxyde métallique est d'abord réduit dans le réacteur à combustibles au contact de combustibles gazeux ou solides (Équation 1.1 dans le cas du méthane et d'un oxyde métallique générique Me_xO_y), puis il est ensuite réoxydé dans le réacteur à air (équation 1.2) au contact de l'oxygène contenu dans l'air (Figure 1.1). Les combustibles ne sont en aucun moment au contact d'oxygène en phase gazeuse et ainsi, les gaz de combustion ne sont pas dilués dans l'azote, ce qui rendrait sa séparation coûteuse.



Les réactions d'oxydations étant exothermiques, on récupère l'énergie dégagée. Le solide est par la suite transféré dans le réacteur à combustibles où il est réduit. Les réactions de réduction (par rapport au solide) peuvent être exo- ou endothermiques, en fonction de l'identité du métal, d'où la présence de la flèche double associée à la chaleur de réduction (Q_{red}) sur

le réacteur à combustibles (Figure 1.1). Par exemple, dans le cas de l'oxyde de nickel (le solide synthétique de référence dans la littérature relative au CLC), les variations d'enthalpies standards des réactions d'oxydation et de réduction (par le méthane) sont respectivement de -240 et 39 kJ mol^{-1} (par mole de métal), alors qu'elles sont plutôt de -156 et -45 kJ mol^{-1} dans le cas de l'oxyde de cuivre (Cu(II)). La variation totale d'enthalpie étant évidemment égale à celle de la réaction globale d'oxydation complète du combustible (-802 kJ mol^{-1} dans le cas de la combustion du méthane).

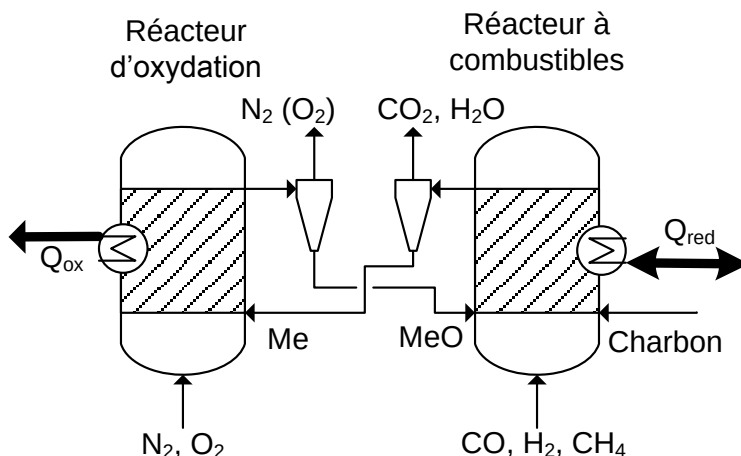


Figure 1.1 Configuration générale du procédé de combustion en boucle chimique dans le cas d'un oxyde métallique générique (Me-O)

1.1.2 Cinétique chimique, hydrodynamique et résistance au transfert de matière

La vitesse d'un processus chimique (c.-à-d. sa cinétique), et son expression mathématique (c.-à-d. sa modélisation) permettent de dimensionner l'équipement dans lequel il sera mené. Or, cette modélisation doit être réalisée à partir de données expérimentales exemptes de déformations dues à la dynamique d'écoulement dans le système réactionnel (l'hydrodynamique), mais aussi dans un régime contrôlé par la cinétique de la réaction (par opposition au transfert de matière interne ou externe). La résistance externe au transfert de matière survient lorsque la cinétique d'une réaction de surface est plus rapide que le transport des réactifs de la phase macroscopique vers le lieu de la réaction, à la surface dans le cas d'un solide. La résistance interne fait référence au transport à l'intérieur du solide par le biais de ses pores ou de sa phase externe déjà consommée. Nous verrons dans le chapitre 5 les critères permettant de s'assurer que les données obtenues au laboratoire sont limitées par la cinétique, et non le transfert de matière.

De façon à acquérir des données cinétiques tout en atténuant les déformations dues à l'écoulement, la minimisation de la taille du réacteur constitue l'approche de choix. Par exemple, dans un Analyseur thermogravimétrique (*Thermogravimetric analyzer*) (TGA), un échantillon de quelques dizaines de milligrammes est soumis à des conditions diverses et la variation de sa masse est mesurée en temps réel. Par contre, plusieurs désavantages résultent de ce type de montage expérimental : la faible quantité de matériel ne garantit pas de la représentativité de l'échantillon, en particulier dans le cas de matériaux hétérogènes comme les minerais broyés. Aussi, le suivi de la variation de la masse ne permet qu'une modélisation amalgamée (*lumped*) du phénomène à l'étude.

Une autre méthode permettant de minimiser les phénomènes hydrodynamiques est d'analyser les gaz produit le plus près possible du lieu de la réaction (p. ex. le lit réactionnel), ou encore d'éliminer les déformations de façon mathématique, c.-à-d. à l'étape de modélisation. L'extraction de la cinétique à partir des données expérimentales (déconvolution) est alors effectuée par le biais d'hypothèse sur l'écoulement (p.ex. réacteur piston), ou alors par la mesure des profils de gaz d'espèces inertes aux conditions d'opération (p. ex. température, pression et concentration), et la modélisation de ces profils. On supposera par la suite que les paramètres de modélisation de ces profils s'appliquent aux espèces réactionnelles aux mêmes conditions opératoires. C'est l'approche retenue dans le présent document.

1.1.3 Modélisation morphologique, mécanistique, empirique et semi-empirique

Il existe plusieurs approches de modélisation de la cinétique d'une transformation chimique. Classiquement, les ingénieurs ont recours aux voies de modélisation empiriques et morphologiques. La modélisation morphologique repose sur l'utilisation d'expressions de la conversion d'un solide à partir d'une liste de fonctions canoniques, que l'on teste jusqu'à identifier celle(s) menant à un ajustement adéquat. Ces fonctions ont été établies sur la base de la modélisation de la germination et la croissance d'une nouvelle phase au détriment de la phase initiale, et de l'avancement du front réactionnel [10]. Il s'agit d'une approche de modélisation particulièrement adaptée aux données acquises sur TGA.

La modélisation mécanistique ou moléculaire cherche plutôt à décrire en détail les phénomènes chimiques en considérant les caractéristiques réelles des solides (défauts ponctuels, sites surfaciques, réseau cristallin, etc.) [10]. On s'attarde ici à la modélisation des phénomènes d'adsorption et de désorption des réactifs et produits, mais aussi de la transformation du solide selon des étapes dites élémentaires, dont la somme conduit à la réaction globale observée. On applique la loi d'action de masse à chacune de ces étapes pour obtenir les expressions mathématiques de la vitesse de celles-ci. Une difficulté de l'approche de modé-

lisation mécanistique se situe au niveau mathématique, en particulier dans le cas de phénomènes transitoires comme la réduction d'oxydes métalliques. Au lieu de ne résoudre que des équations différentielles ordinaires comme dans le cas de la modélisation morphologique, les bilans à résoudre font appel à des systèmes couplés d'équations aux dérivées partielles. Finalement, on distingue les modèles cinétiques empiriques ou semi-empiriques. Ces modèles visent l'ajustement de courbes, sans tentative d'explication du phénomène à l'étude, c.-à-d. sans significations sur les mécanismes en jeu. Le modèle le plus utilisé est celui de loi de puissance, où on cherche à quantifier les exposants attribués aux concentrations des espèces dans la phase gazeuse. Dès lors, l'extrapolation de ces modèles est sujette à caution.

1.2 Éléments de la problématique

Ce projet d'études doctorales a été réalisé en continuité avec ceux qui ont mené à une maîtrise, dans lesquels des porteurs d'oxygène d'origine minérale ont été identifiés. En particulier, les travaux de recherches de maîtrise [11] ont permis d'identifier la pyrolusite, un oxyde de manganèse de formule moléculaire MnO_2 , ce qui a mené au dépôt d'un brevet conjoint entre Polytechnique Montréal, Total et l'IFP-EN concernant l'activation de ce porteur [12]. La suite logique de ce projet, dans une optique d'éventuel dimensionnement de procédé pilote et/ou industriel consiste à modéliser les cinétiques de réduction des meilleurs porteurs d'oxygène d'origine minérale : soit la pyrolusite (identifiée par l'auteur de ce document), et l'ilménite (le solide d'origine minérale de référence dans la littérature). L'obtention de modèles cinétiques pour la réduction de ces deux oxydes permettra d'identifier les mécanismes permettant d'expliquer les différentes vitesses de réduction.

De façon à circonscrire les travaux de modélisation, nous avons opté pour la modélisation des réactions de réduction de ces oxydes par le monoxyde de carbone. En effet, en plus de constituer un des réactifs présents dans les gaz de synthèse (un combustible envisagé pour la CLC [13, 14]), le monoxyde de carbone constitue un des réactifs intermédiaires générés lors de la carboréduction, c.-à-d. lors de la réduction à l'aide de charbon, soit le combustible le plus probable pour la mise à l'échelle industrielle du procédé CLC. Par contre, en plus de la réduction par le monoxyde de carbone, une caractérisation préliminaire (analyse des mécanismes réactionnels, capacité de transfert d'oxygène) est fournie pour la réduction de la pyrolusite par l'hydrogène, le méthane, ainsi que des mélanges hydrogène-méthane et monoxyde de carbone.

L'approche mécanistique de modélisation cinétique est utilisée dans ce document. Ce choix repose sur les résultats de travaux de modélisation préliminaire (et discuté dans les chapitres 1 et 2) : l'approche morphologique habituellement favorisée par les ingénieurs mène à des

solutions multiples. En testant tour à tour les fonctions canoniques exprimant l'évolution de la morphologie du solide en fonction de sa conversion, on arrive à ajuster les mêmes données expérimentales à l'aide de plusieurs modèles de natures contradictoires (p. ex. modèle à coeur rétrécissant (*shrinking core*), loi de puissance exprimant un phénomène de surface ou encore modèle de diffusion). La raison de cette multiplicité réside potentiellement sur le non-respect des hypothèses ayant menées à ces fonctions canoniques : des phénomènes de germination et croissance sur l'ensemble du volume par opposition aux phénomènes surfaciques types des réactions gaz solide, croissance sans fin des nouvelles phases formées (sans arrêt aux interfaces germes-germes, à la surface des solides, etc.) [15].

1.2.1 Cinétique de la réduction de l'ilménite pré-oxydée

L'ilménite est un oxyde mixte de fer et titane de formule moléculaire FeTiO_3 , identifié dans la littérature comme le solide de référence d'origine minérale pour le procédé CLC. Il s'agit d'un remplaçant potentiel pour les oxydes de synthèse à base de nickel identifiés par différents groupes de recherche. Or, cet oxyde présente plusieurs limitations, malgré une tenue mécanique exemplaire et une absence de toxicité. La pseudobrookite ferrique (Fe_2TiO_5), la forme oxydée de l'ilménite, ne peut théoriquement transférer que 5 % de sa masse en oxygène (capacité de transfert d'oxygène). Ce faisant, 95 % de sa masse constitue une masse thermique inerte, même si une partie de cette masse thermique sert à transférer de la chaleur entre le réacteur d'oxydation et celui de réduction. Aussi, en raison de cette faible capacité de transfert d'oxygène, un inventaire considérable est à envisager dans le cas d'un éventuel procédé de taille industrielle, avec les dimensions titanesques de réacteurs que cela entraîne. Aussi, cet oxyde est sujet à l'agglomération par frittage. Le frittage survient autant lors de la préoxydation initiale (quelques heures sous air à 800-1000 °C) permettant d'augmenter de 2 % sa capacité de transfert d'oxygène, ou encore lors de réductions aussi courtes que 5 min sous méthane [11].

Finalement, il convient de noter que la cinétique publiée de réduction de l'ilménite préoxydée est contradictoire en fonction des auteurs l'ayant étudiée. La réduction de l'ilménite préoxydée sous monoxyde de carbone a été caractérisée tour à tour à l'aide de modèles à coeur rétrécissant en 1 [16] ou 3 dimensions [17, 18], ou encore comme un phénomène de surface [19]. Ce faisant, les ordres de réaction et les énergies d'activation publiées varient considérablement : de 0,7 à 1,9 pour les ordres de réaction par rapport au monoxyde de carbone, et de 20 à 113 kJ mol⁻¹ pour les énergies d'activation. Ainsi, pour être en mesure de proposer un oxyde minéral de remplacement à l'ilménite, il convient d'abord de lever les incertitudes sur la cinétique de réduction sous CO.

1.2.2 Cinétique de la réduction de la pyrolusite calcinée

Nous avons préalablement identifié la pyrolusite comme porteur d'oxygène de remplacement pour le procédé CLC sur la base de la masse d'oxygène transféré du solide vers le gaz [11], sans toutefois caractériser sa cinétique de réduction. En fait, aucun modèle cinétique n'a été publié pour la pyrolusite à notre connaissance. Seules quelques études sur la première réduction d'oxydes de manganèse de synthèse [20, 21, 22] et de minerais [23, 24] ont été publiées, donc dans le contexte métallurgique d'obtention de métaux. Or, dans la CLC, l'oxyde est séquentiellement oxydé et réduit, sur des centaines de cycles. Donc, de ce point de vue, la première réduction est peu intéressante (et ces données ne sont habituellement pas considérées pour la modélisation) car non représentative de l'état du porteur d'oxygène sur sa durée de vie dans le procédé. Ainsi, la caractérisation cinétique de la réduction de la pyrolusite par le monoxyde de carbone sera réalisée pour pallier cette lacune.

1.2.3 Quantification des paramètres cinétiques de surface des oxydes

La modélisation cinétique par voies mécanistiques entraîne la nécessité de quantifier certains paramètres de surface. Les taux de réaction et bilans sur les espèces surfaciques font intervenir ces quantités, et la quantification de ceux-ci (p. ex. concentration surfacique de sites) n'est pas aisée. Les méthodes de caractérisation sont peu nombreuses [25, 26, 27] et doivent être réalisées à des conditions le plus près possibles de celles dans lesquelles se déroulent les processus étudiés. De plus, certaines méthodes impliquent la manipulation de produits chimiques pyrophoriques [25]. Aussi, les méthodes de titration gaz-solide sont inapplicables à haute température : l'oxygène du réseau cristallin, en plus de l'oxygène de surface, participe aux réactions de réduction. La quantification de la densité surfacique de sites sera envisagée du point de vue de la modélisation. Les valeurs calculées seront par la suite comparées aux données publiées afin de s'assurer de leur justesse.

1.2.4 Intégration du CLC et des cycles à carbonate

Les éléments de la problématique discutés jusqu'à maintenant circonscrivent l'enveloppe du projet à la seule caractérisation du minerai utilisé comme porteur d'oxygène. Or, de façon à tirer profit de certaines propriétés du procédé CLC, plusieurs auteurs ont proposé d'y intégrer les cycles de captation de CO_2 [28, 29] dans un contexte de production d'hydrogène. En effet, la production d'hydrogène, que ce soit à partir du procédé de reformage du méthane ou encore par gazéification du charbon, passe par une étape de purification par enlèvement du CO_2 dans des réacteurs où se déroule la réaction d'échange gaz-eau (*water-gas shift*). Or, les technologies

d'enlèvement du CO_2 ont toutes des inefficacités inhérentes : les gaz de combustion doivent être refroidis à des températures allant de 10 à 40 °C pour être alimentés à une tour de lavage, puis la solution de lavage est régénérée à haute température. La consommation de vapeur pour la régénération entraîne une pénalité de 12 à 16 % [6].

L'utilisation d'un accepteur de CO_2 capable de fonctionner à haute température contribue à augmenter l'efficacité globale du procédé, en plus de déplacer l'équilibre de la réaction d'échange gaz-eau vers la production d'hydrogène et de fournir une partie de l'énergie nécessaire au reformage (réaction exothermique de carbonatation couplée à la réaction endothermique de reformage). Dans les cycles à carbonate, la chaux (CaO) est carbonatée à haute température (jusqu'à environ 650 °C), puis régénéré à des températures allant jusqu'à 1000 °C. Pour fournir la chaleur nécessaire à la régénération, on fait appel à une réaction de combustion. Or, dans un contexte de séquestration de CO_2 , la régénération doit être réalisée en absence d'azote (oxycombustion). Or, en couplant le CLC et les cycles à calcium (Cycles à calcium (*Calcium looping*) (CaL)), la chaleur dégagée par la réduction de la phase oxyde de cuivre d'un oxyde mixte cuivre-calcium permet de régénérer l'oxyde de calcium via la décomposition thermique de la carbonate de calcium formée lors de la captation du CO_2 . Ainsi, la faisabilité de l'intégration réside sur l'obtention d'une cinétique adéquate de captation de CO_2 d'un oxyde mixte calcium et porteur d'oxygène.

1.3 Objectifs de recherche

En fonction des différents éléments exposés dans la sous-section précédente, les objectifs de recherche sont les suivants :

1. Modéliser la densité surfacique de sites actifs d'oxydes d'origine minérale ;
2. Caractériser la cinétique de réduction de l'ilménite secondaire préoxydée par le monoxyde carbone ;
3. Caractériser la cinétique de réduction de la pyrolusite calcinée par le CO ;
4. Comparer les cinétiques de réduction par le CO et identifier l'oxyde le plus réactif ;
5. Caractériser le potentiel de réduction du dioxyde de carbone en monoxyde de carbone de la pyrolusite ;
6. Caractériser la cinétique de captation de CO_2 d'un oxyde mixte d'oxyde de calcium (CaO) et porteur d'oxygène ;

CHAPITRE 2 REVUE DE LITTÉRATURE

2.1 Combustion en boucle chimique

L'idée de la CLC est née en 1954 lorsque Lewis and Gilliland [30] du Massachusetts Institute of Technology (MIT), déposent un brevet pour un procédé de production de dioxyde de carbone pur. Puis à partir des années 1980, le procédé CLC (dont le nom apparaît pour la première fois en 1987 [31]) subit un développement accéléré axé sur la production d'énergie. Depuis 1994, des grands groupes industriels ont financé le développement du procédé (p. ex. Total [32, 33, 34, 35, 12, 36, 37, 38, 39], Alstom Technology [40, 41, 42, 43, 44, 45, 46, 47], Mitsubishi Hitachi Power Systems [48, 49, 50, 51], Saudi Arabian Oil [52, 53, 54] et Shell [55, 56, 57, 58]), contribuant du même coup à une multiplication des publications : plus de 1600 articles publiés depuis 1994, avec plus de 300 publications pour l'année 2014, et un nombre moyen de 18,12 citations par article. Les articles publiés touchent autant le développement de porteurs d'oxygène, les configurations du procédé, les différents types de combustibles, de même que l'effet des conditions d'opérations (température, pression, etc.) sur les performances du procédé. Par contre, l'essentiel des efforts de développement porte sur la sélection de porteurs d'oxygène synthétiques.

Mis à part la production d'énergie, le principe de boucle chimique est mis à profit pour favoriser un extrant en particulier (énergie, hydrogène, etc.). Par exemple, on peut produire de l'hydrogène en remplaçant l'air du réacteur d'oxydation par de la vapeur d'eau [59] ou encore en ajoutant un réacteur intermédiaire de clivage d'eau (*water splitter*) avant le réacteur d'oxydation [60, 61, 62, 63, 64, 60, 65, 66]. Ces modifications sont possibles dans la mesure où le porteur d'oxygène peut réduire la vapeur d'eau (oxydes de fer). On peut également favoriser la production de gaz de synthèse par reformage du méthane [59, 67, 68] ou par clivage d'eau réduction du dioxyde de carbone [69], ou encore par gazéification de combustibles solides (biomasse, charbon) en boucle chimique (Gazéification en boucle chimique (*Chemical looping gasification*) (CLG)) [70, 71]. Dans cette configuration, le combustible solide est gazéifié au contact d'un oxyde métallique, donc sans apport d'air ou d'oxygène en phase gazeuse [72].

Le réacteur à combustibles sert à convertir des combustibles gazeux (méthane [73, 74, 75, 76, 77, 78] ou solides (charbon [79, 80, 51, 81, 72]) tout en générant un courant gazeux ne contenant que du dioxyde de carbone et de l'eau. Par contre, dans les publications récentes, les auteurs se sont penchés sur des combustibles alternatifs : biomasse telle la balle de riz [82], glycérol [66], fraction lourde de biohuile [83]. De même, des travaux récents ont permis de démontrer la possibilité de séquestrer le CO_2 généré dans le réacteur à combustibles *in situ*

par formation de carbonates à l'aide d'un oxyde mixte contenant du calcium, ce qui a mené au couplage du procédé CLC avec les cycles à carbonates (CaL). Dans ce procédé combiné, on utilise un oxyde mixte cuivre/calcium. La chaleur dégagée par la réoxydation de l'oxyde de cuivre permet d'atteindre la température de décomposition du carbonate de calcium et régénère ainsi l'oxyde de calcium. Tout comme pour le procédé CLC, l'essentiel des travaux de recherche porte sur l'amélioration du solide utilisé, soit au niveau des performances de carbonatation par ajout de promoteurs [84], par l'établissement du ratio optimal d'oxyde de cuivre et de calcium [85], ou encore au niveau de la tenue mécanique à l'aide de supports alternatifs [84].

Plusieurs modes d'opération ont été proposés pour le procédé. Malgré que certains auteurs aient proposé une opération en lit fixe en raison de la facilité du passage d'une atmosphère réductrice à oxydante, c.-à-d. par simple modification des gaz alimentés [86]. [87, 88, 86, 59], la configuration lit fluidisé circulant a été graduellement adopté [89, 90, 65, 88, 49]. Dans celle-ci, le réacteur à combustibles est opéré en régime bullant, alors que le réacteur d'oxydation est constitué d'une colonne de montée (*riser*). Les avantages des réacteurs à lit fluidisé sont nombreux : transfert de chaleur et de matière supérieurs (par comparaison aux lits fixes), facilité de circulation du solide en raison de l'état de fluidisation, absences de pièces mécaniques internes, uniformité de l'état d'oxydation du solide dans le lit [91], sélectivité soutenue, conversion du méthane, résistance au cokage et plus grande efficacité thermique) [88] pour ne citer que ceux-ci. Par contre, la circulation du solide entre les réacteurs et l'étanchéité des réacteurs par rapport aux gaz entraînent des complications techniques [88].

2.1.1 Porteurs d'oxygène

Le développement et la sélection de porteurs d'oxygène ont caractérisé les phases initiales de développement du procédé, et continue de constituer l'essentiel des efforts de recherche, comme en témoigne le nombre de publications sur ce sujet : plus de 700 publications portant sur des porteurs d'oxygène potentiels. Ceux-ci doivent présenter une grande réactivité, être chimiquement (désactivation) et thermiquement stables (propension à l'agglomération), posséder une tenue mécanique adéquate (résistance à l'attrition), et ne pas favoriser la décomposition thermique du combustible par cokage. Ils doivent également être de toxicité minimale, abondants et peu chers. La réactivité d'un oxyde est souvent analysée en termes de capacité de transfert d'oxygène, soit la quantité d'oxygène transférée lors de la réduction du solide, par masse initiale de solide.

Les oxydes de synthèse les plus étudiés dans la littérature sont ceux à base de fer, nickel, cuivre, calcium, cobalt et manganèse (tableau 2.1). L'évaluation des performances des por-

teurs d'oxygène et leur comparaison sont rendues difficiles en raison de la pluralité des critères retenus. Les performances des porteurs d'oxygène sont évaluées dans plusieurs cas à l'aide de notion floue de réactivité, sans homogénéité entre les paramètres évalués à travers les différentes publications (conversion absolue/relative du solide, transfert d'oxygène sur une base massique, comparaison du profil des gaz de combustion, confusion entre conversion du solide et conversion des gaz). Or, autant la conversion du solide que celles des gaz constituent une propriété du système réactionnel à l'étude. La conversion des gaz dépend entre autres, de la quantité de gaz alimenté, tout comme la conversion du solide dépend du solide en question, de la température et de l'agent réducteur utilisé. De même, le recours au concept de capacité de transfert d'oxygène comme critère de performance entraîne son lot de difficultés : pour des porteurs d'oxygène à base du même oxyde, plusieurs paramètres peuvent influencer les valeurs de capacité de transfert d'oxygène : méthode de préparation (extrusion, imprégnation humide, coprécipitation, etc.), température de calcination [92], nature de l'agent réducteur (CO/H_2 , CH_4 , charbon, présence de soufre, etc.), etc. Ceci dit, les oxydes de nickel ont démontré leur supériorité en termes de capacité de transfert d'oxygène et se sont imposés comme solides de référence du procédé CLC.

Mis à part les oxydes de synthèse, les minerais sont d'un intérêt certain pour assurer la faisabilité économique et le déploiement du procédé CLC à l'échelle industrielle. Les coûts inhérents de séparation du CO_2 et de l'air par le procédé en boucle chimique sont de 14 à 28 \$ (CAD) par tonne lorsque l'on compare la combustion du charbon et son équivalent CLC [131]. En effet, en raison de l'opération en régime de fluidisation, des pertes de porteurs d'oxygène par attrition sont inévitables. De plus, la nature cyclique des réactions entraîne une dégradation graduelle des propriétés mécaniques. Aussi, la désactivation des porteurs risque de survenir, que ce soit par agglomération (frittage ou encore en raison de la présence de sodium dans les combustibles solides) ou par empoisonnement chimique (p.ex. présence de soufre dans les combustibles) [132]. Ainsi, un remplacement des oxydes doit être assuré. Pour minimiser les coûts de remplacement du porteur, et pour combler la différence entre la combustion classique et le CLC, une stratégie consiste à minimiser le coût des porteurs d'oxygène. Or, les minerais ont des coûts évidemment inférieurs aux porteurs d'oxygène de synthèse (pour un métal donné). Certains sous-produits ou déchets industriels ont également été envisagés comme porteurs d'oxygène (p. ex. résidus de bauxite pour la gazéification du charbon [133]). Dans ce cas, la disposition finale doit être envisagée de façon à éviter une contamination de l'environnement [134].

Depuis le début du développement du procédé, l'utilisation de minerais des mêmes métaux a été envisagée. Par exemple, plusieurs auteurs se sont intéressés à l'utilisation de l'hématite (Fe_2O_3) : pour la gazéification de charbon [80, 135, 136, 137], la combustion du méthane [137].

Tableau 2.1 Porteurs d'oxygène de synthèse utilisés dans le procédé CLC.

Phase active	Support	Références
CeO ₂		[93]
Co ₃ O ₄	Al ₂ O ₃ TiO ₂	[94, 95] [96]
CuO	Al ₂ O ₃ SiO ₂ Mg ₄ Si ₆ O ₁₅ (OH) ₂ 6H ₂ O TiO ₂	[92, 97, 98, 99, 100, 101, 102, 95] [92, 99, 103] [92, 99] [92, 99, 104]
Fe ₂ O ₃	Al ₂ O ₃ SiO ₂ Mg ₄ Si ₆ O ₁₅ (OH) ₂ 6H ₂ O TiO ₂ MgAl ₂ O ₄ ZrO ₂	[92, 105, 97, 106] [105] [105] [107, 105, 97, 108] [109] [61]
Mn ₂ O ₃	Al ₂ O ₃ SiO ₂ Mg ₄ Si ₆ O ₁₅ (OH) ₂ 6H ₂ O TiO ₂ ZrO ₂ MgZrO ₂ CaO/ZrO ₂ CeO/ZrO ₂	[105, 95] [105] [105] [105] [110] [111, 112] [110] [110]
Mn ₃ O ₄		
NiO	Al ₂ O ₃ SiO ₂ Mg ₄ Si ₆ O ₁₅ (OH) ₂ 6H ₂ O TiO ₂ MgAl ₂ O ₄ CaAl ₂ O ₄ YSZ Bentonite	[92, 112, 113, 114, 115] [116, 117, 118, 119, 120] [121, 122, 123, 95] [92] [92] [92, 124] [113, 118, 125, 126, 127] [118, 125] [122] [128, 129, 130]

Des capacités de transfert d'oxygène de 9 % ont été mesurées sur TGA lors de la réduction de l'hématite par le méthane durant 15 min [137].

Des minerais de manganèse (pyrolusite, psilomélane) ont également été étudiés pour la réduction du méthane dans le procédé CLC [138, 11, 139]. En calcinant la pyrolusite sous une pression partielle d'oxygène élevée, on peut doubler la capacité de transfert d'oxygène (par rapport à une calcination sous inerte)[11]. Linderholm et al. [139] ont testé l'effet de l'ajout de chaux vive (CaO) sur les propriétés mécaniques d'un oxyde de manganèse en provenance du Brésil (initialement majoritairement constitué de MnO_2 amorphe) lors de la combustion de coke de pétrole (*petcoke*). Ils ont conclu en une augmentation de la conversion autant des combustibles gazeux (syngaz) que solides (par rapport à l'ilménite). L'ajout de chaux vive n'a malheureusement pas amélioré la résistance à l'attrition de l'oxyde de manganèse.

Des oxydes mixtes fer-manganèse ont également été envisagés, avec des contenus en manganèse situés entre 0 et 39 % [131]. Les plus hautes capacités de transfert d'oxygène ont été obtenues avec le minerai à haute teneur en manganèse (3 %) lors de réduction sous hydrogène, alors que lors de la réduction sous méthane, celui sans manganèse a présenté les meilleures performances.

L'oxyde mixte de référence du procédé demeure l'ilménite, un oxyde de fer et titane (FeTiO_3 , ou encore $\text{FeO} \cdot \text{TiO}_2$). Il est de loin le minerai le plus étudié [140, 11, 141, 142, 137, 139]. L'ilménite s'est graduellement comme solide de référence dans le procédé CLC. En effet, malgré une capacité de transfert d'oxygène limitée, l'ilménite présente une résistance à l'attrition élevée. Il s'agit d'un oxyde robuste, c.-à-d. résistant face à la désactivation chimique due au soufre [132]. Or, son coût est pourtant élevé en raison de son utilisation pour la production de pigment (TiO_2).

Les minéraux et résidus industriels testés comme porteurs d'oxygène potentiels pour le procédé CLC sont présentés dans le tableau 2.2.

Tableau 2.2 Minerais et résidus testés en tant que porteurs d'oxygène dans le procédé CLC.

Element	Minerais	Formule moléculaire	Référence
Be	Béryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	[11]
Co	Cobaltite	CoAsS	[11]
Cu	Cuprite	Cu_2O	[11, 137]
	Chrysocolle	CuO	[137]
	Malachite	$\text{CuO}/\text{Fe}_2\text{O}_3$	[137]
Fe	Ilménite	FeTiO_3	[11, 141, 132, 131, 140, 142, 139]
	Hématite	Fe_2O_3	[143, 11, 80, 136, 135, 131, 137]
	Magnétite	Fe_3O_4	[11, 137]
	Limonite	$\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$	[11, 137]
Mg	Brucite	$\text{Mg}(\text{OH})_2$	[11]
Mn	Pyrolusite	MnO_2	[11, 138]
	Psilomélane	$(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$	[11]
Ni	Millerite/Pentlandite	$(\text{Fe}, \text{Ni})_9\text{S}_8$	[11]
V	Vanadinite	$\text{Pb}_5\text{Cl}(\text{VO}_3)$	[11]
	Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$	[11]

2.2 Cinétique de réduction d'oxydes métalliques dans le domaine de la CLC

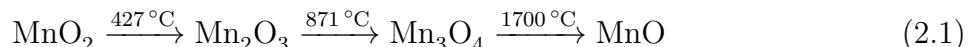
Malgré le nombre considérable de publications portant sur la caractérisation de la réactivité de porteurs d'oxygène, celles portant sur la caractérisation et la modélisation des cinétiques de réduction de ces solides demeurent peu nombreuses. En plus du faible nombre de publications sur le sujet, certaines d'entre elles ne s'intéressent qu'à une analyse descriptive des mécanismes réactionnels les plus probables (p. ex. passage direct ou non d'une phase cristallographique à une autre, formation de carbone sur les porteurs lors de la réduction [144, 145], vitesse apparente de réaction sur la base du profil de conversion, etc.), sans proposer de modèle cinétique. Certains auteurs proposent même des modèles cinétiques à partir de données expérimentales brutes obtenues sur lit fluidisé [146] ou sur certains montages expérimentaux sophistiqués [147], sans pour autant considérer de modèles hydrodynamiques. Finalement, la majorité des modèles cinétiques sont élaborés à partir de données obtenues sur analyseurs thermogravimétriques alors que le mélange gaz-solide est limité.

La modélisation cinétique a traditionnellement été envisagée du point de vue des mécanismes réactionnels dits mécanistiques (loi d'action de masse appliquée à des étapes élémentaires d'un mécanisme global). Par contre, la modélisation ne faisant appel qu'aux changements morphologiques d'un solide, c.-à-d. les modèles morphologiques, a remplacé cette façon de faire. Pour cause, les modèles morphologiques canoniques (une vingtaine) sont testés à tour

de rôle, et un modèle est sélectionné comme représentatif lorsque l'ajustement de courbe est jugé satisfaisant (sur la base du coefficient de corrélation par exemple). Le domaine de la boucle chimique ne fait pas exception et on remarque que l'entièreté des publications sur la caractérisation cinétique est le fait de modélisations morphologiques (tableau 2.3). La nomenclature utilisée est explicitée dans le tableau 6.1. Or, nous verrons que cette famille de modèles relève plutôt de l'ajustement de courbe, et qu'il est possible d'ajuster les données sur plusieurs modèles alors que certains décrivent des phénomènes surfaciques, d'autres de diffusion ou de coeur rétrécissant. Or, en consultant les publications citées, on constate que les auteurs ont passé sous silence cet aspect, et que des modèles différents ne semblent pas avoir été testés et que le choix du modèle repose sur des analyses de micrographies ou encore des préférences d'auteurs.

2.2.1 Réduction d'oxydes de manganèse

Les oxydes de manganèse se présentent sous plusieurs formes : MnO_2 , Mn_2O_3 , Mn_3O_4 et MnO . Stobbe et al. [159], entre autres, ont identifié les phases prépondérantes en fonction de la température lors d'une calcination sous air (équation 2.1). Ce schéma est réversible, sauf pour le retour à la phase initiale MnO_2 , à moins d'être à des conditions de pressions d'oxygène très élevées (p. ex. 3000 bar sous oxygène pur [159]). Aussi, ce schéma n'identifie que la phase prépondérante, mais sans exclure la coexistence de ces phases à des conditions données. Par exemple, nous verrons que la décomposition de la pyrolusite (MnO_2) par calcination ou par réduction vers 530°C génère un mélange des phases Mn_2O_3 , Mn_3O_4 et MnO , dont la prépondérance est fonction de la pression partielle d'oxygène.



Les catalyseurs à base de manganèse sont connus depuis longtemps pour leur capacité à convertir le CO en CO_2 en présence d'oxygène moléculaire : les catalyseurs hopcalites (oxydes mixtes manganèse-cuivre) ont été conçu pour la purification de l'air à température ambiante dans les sous-marins [160]. Les études cinétiques d'oxydation du monoxyde de carbone avec oxygène coalimenté sur un catalyseur à base de manganèse à basse température abondent : purification de courant gazeux d'hydrogène pour des piles à combustible [161, 162], catalyseurs pour pots d'échappement [163], etc. Or, elles sont peu nombreuses pour l'oxydation du CO sans oxygène en phase gazeuse (consommation de l'oxygène du solide) à des températures supérieures à 600°C .

Parmi les rares études de réduction à haute température, aucune ne s'intéresse à la modéli-

Tableau 2.3 Modèles cinétiques publiés de réduction de porteurs d'oxygène.

Porteur d'oxygène	Réducteur	Modèle cinétique	Références
CaSO ₄	H ₂	A2	[148]
	CO	F1	[149]
Fe ₂ O ₃	charbon	Pores aléatoires	[89]
	CH ₄	D3	[150]
Fe ₂ O ₃ /Al ₂ O ₃	CO+H ₂	R3	[92]
	CO, H ₂ et CH ₄	R3	[151]
FeTiO ₃	CO, H ₂ et CH ₄	R3	[17]
	CO	R1/R3	[18, 16]
MnFe ₂ O ₄	CH ₄	D3	[150]
ZnFe ₂ O ₄	CH ₄	F1	[150]
CuO	CO	Loi de puissance empirique	[152]
CuO/Al ₂ O ₃	CO+H ₂	R3	[92]
	CO, H ₂ et CH ₄	F0/R1	[153]
	CO, H ₂ et CH ₄	F0/R1	[151]
	CO	R3	[154]
NiO/Al ₂ O ₃	CO+H ₂	R3	[92]
	CH ₄	F1	[155, 156]
	CO, H ₂ et CH ₄	R3	[151]
NiO/bentonite	CH ₄	R3/D	[129]
NiO/YSZ	CH ₄	Loi de puissance empirique	[157]
Co-Ni/Al ₂ O ₃	H ₂	F1	[147]
La-Ni/Al ₂ O ₃	H ₂	F1	[158]

sation cinétique du phénomène. Stobbe et al. [159] a caractérisé les changements de stoechiométrie d'oxydes de manganèse de synthèse lors de la première réduction sous H_2 et CH_4 à température croissante (TPR). Ils ont noté que le Mn_2O_3 est réduit en deux étapes (formation de Mn_3O_4 suivi de MnO) et que ces phénomènes sont identiques, sauf qu'ils surviennent à 200 °C plus élevé dans le cas de la réduction sous CH_4 . Aussi, ces auteurs ont pu valider le cokage négligeable lors de la réduction sous méthane durant 20 h à 830 °C. Ils ont mesuré des taux de cokage variant de l'ordre de 0,15 %, sans préciser s'il s'agissait d'un ratio carbone/masse initiale d'oxyde, ou encore de fraction du carbone alimenté.

Dans le domaine de la CLC, plusieurs chercheurs se sont intéressés aux oxydes de manganèse pour une application avec relargage en phase gazeuse de l'oxygène du réseau cristallin (Boucle chimique avec relargage de l'oxygène en phase gazeuse (*Chemical looping with Oxygen Uncoupling*) (CLOU)) [164, 165]. L'intérêt de cette configuration du procédé CLC réside surtout au niveau de la conversion de combustible solide. La génération d'oxygène en phase gazeuse permet d'augmenter la vitesse de réaction de combustion, autrement très lente (solide-solide). En plus de l'intérêt pour les oxydes de manganèse de synthèse, les minerais de manganèse ont aussi attiré l'attention des chercheurs [166, 167, 168, 139, 169], en particulier pour la conversion de CO et H_2 [170]. Des taux élevés d'attrition ont été mesurés pour les minerais de manganèse, et plusieurs stratégies ont été envisagées : mélange d'oxyde de manganèse avec des oxydes de fer [169], imprégnation à sec de cuivre [171, 172]. Des minerais de manganèse avec un contenu en potassium élevé permettent d'obtenir des taux de gazéification de charbon plus élevée qu'avec l'ilménite, en plus d'être disponible à une fraction du coût de celle-ci [167]. Malheureusement, la majorité des auteurs se contente de présenter des résultats bruts sans proposer de modélisation cinétique.

CHAPITRE 3 COHÉRENCE DES ARTICLES PAR RAPPORT AUX OBJECTIFS DE LA RECHERCHE

Le chapitre 2 proposait une revue de la littérature, couvrant à la fois une brève présentation du procédé et de ses récents développements, de même que les porteurs d'oxygène les plus prometteurs. Une emphase particulière a été mise sur la modélisation cinétique de la réduction de ces porteurs d'oxygène dans le contexte de la CLC, c.-à-d. dans le contexte de cycles d'oxydoréduction répétée de ceux-ci, très différents des travaux similaires réalisés en métallurgie (réduction unique en vue de la production de métaux, sans dégradation graduellement des propriétés mécaniques des oxydes, etc.). La comparaison des différents modèles cinétiques proposés dans la littérature, peu nombreux, mais contradictoires, justifiera la pertinence de proposer un modèle alternatif permettant de caractériser la cinétique de réduction de l'ilménite, le porteur d'oxygène de référence jusqu'à maintenant, sur la base d'une méthode rigoureuse de modélisation mécanistique. Le modèle développé sera présenté au chapitre 4 (article publié dans le volume 165 (2016) de la revue *Fuel* [141]).

De façon à proposer un porteur d'oxygène permettant de diminuer l'inventaire de solides requis dans le cadre d'un déploiement industriel du procédé CLC, nous caractériserons la cinétique de réduction de la pyrolusite, un des porteurs d'oxygène que nous avons préalablement identifié dans le cadre de travaux de maîtrise. Le modèle de réduction de la pyrolusite calcinée par le monoxyde de carbone sera présenté au chapitre 5 (article publié dans le volume 295 (2016) du *Chemical Engineering Journal* [173]).

L'analyse des courbes de réduction de la pyrolusite sous concentration croissante de monoxyde de carbone nous permettra de proposer une méthode alternative de caractérisation de certains paramètres de surface apparaissant dans les expressions des taux de réaction établies sur la base d'une approche de modélisation mécanistique. En effet, nous proposerons dans le chapitre 5 une méthode de simulation de la titration d'une surface par une substance agissant à la fois comme sonde et agent réducteur. La méthode proposée permet de répondre aux critères de détermination de la densité surfacique de sites actifs : soit la caractérisation dans des conditions le plus près possibles des conditions expérimentales, de même que l'utilisation du réactif chimique comme sonde de mesure. Nous verrons aussi la possibilité de modéliser la densité surfacique de sites actifs dans le cadre de la modélisation cinétique. Nous verrons également dans le chapitre 5 qu'il est possible d'estimer cette quantité en la définissant comme un paramètre d'ajustement de courbe.

Finalement, nous nous intéresserons dans les chapitres 6 et 7 à certaines améliorations à

apporter au procédé CLC. Premièrement, le chapitre 6 présente la possibilité de l'ajout d'un réducteur de dioxyde de carbone et d'eau dans le but de produire du monoxyde de carbone et de l'hydrogène à partir des gaz de combustion à partir de la pyrolusite soumise à une centaine de cycles d'oxydoréduction. Ce faisant, nous verrons que la production de gaz de synthèse ne se fait pas au détriment de l'extrait énergétique du procédé, comme dans les configurations alternatives proposées par certains auteurs. Ce chapitre est un article ayant été publié dans le volume 94 du *Canadian Journal of Chemical Engineering* [69].

Le chapitre 7 présente la possibilité de captation *in situ* du CO_2 par l'utilisation d'un oxyde mixte dans le contexte combiné de la CLC et des cycles à calcium (formation de carbonate de calcium) pour la production d'hydrogène. En effet, en combinant un oxyde de cuivre et un oxyde de calcium, on peut améliorer l'efficacité de l'enlèvement du CO_2 des gaz de reformage à haute température, et sans faire appel aux réaction d'oxycombustion pour la régénération de la chaux. Le chapitre 7 est un article ayant été soumis au *Chemical Engineering Journal*.

Nous concluons la thèse par une discussion synthèse sur l'ensemble des travaux de ce doctorat, et une conclusion générale. Il sera également question dans la discussion de quantifier l'inventaire de solides nécessaires dans le réacteur à combustible dans le cas du remplacement de l'ilménite par la pyrolusite, et de discuter de façon préliminaire d'une stratégie d'intégration des propriétés de réduction du CO_2 et du clivage d'eau de la pyrolusite dans le procédé CLC. Nous espérons sincèrement que ces travaux aideront dans la compréhension générale de la modélisation cinétique dans un contexte mécanistique classique (et facilitera le travail de quantification de paramètres de surfaces comme la densité surfacique de sites actifs), tout en contribuant à un éventuel déploiement commercial du procédé CLC.

CHAPITRE 4 ARTICLE 1 : ILMENITE–CO REDUCTION KINETICS

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Article publié dans la revue *Fuel* [141]

Abstract

Secondary ilmenite is an inexpensive mineral that is a potential oxygen carrier for the chemical looping process. It has excellent mechanical stability, adequate heat capacity to transfer heat from the air reactor to the fuel reactor, and possesses a modest oxygen transfer capacity. Fresh and preoxidized ilmenite can transfer up to 1,7 % and 1,2 % oxygen on a mass basis, when reduced for 2 min with CO at 910 °C. Preoxidizing ilmenite reduces its tendency to agglomerate but it also reduced its reactivity towards CO. We characterized the kinetics of the reduction of preoxidized secondary ilmenite from South Africa with a mechanistic model. The model assumes CO reacts with surface oxygen atoms, and that bulk oxygen replenishes the surface oxygen. The model accounts for more than 90 % of the variance in the data. The activation energies of the surface reduction and reoxidation steps are 51 kJ mol⁻¹ and 89 kJ mol⁻¹, respectively. The surface site density decreases with the reduction cycles via the simple power law expression because sintering deactivates the catalyst.

4.1 Introduction

Chemical looping literature is vast with over 500 publications since 1994. Many of these papers devote their attention to the synthesis of oxygen carriers, evaluating their performance (reactivity studies, conversion and stability), and identifying the morphological structure with advanced spectroscopic analytical techniques. Oxygen carriers should have a high oxygen transfer capacity (mass of transferable oxygen per mass of carrier) to minimize the solid inventory, high mechanical resistance, adequate specific heat capacity to transport heat from the air to the fuel reactor, in addition to being inexpensive. Since capturing and sequestering CO₂ has little intrinsic value (except in the case of carbon dioxide flooding for enhanced oil recovery), minimizing oxygen carrier cost has been a significant factor in developing the process. Due to their low cost, many minerals were studied for their reactivity : ilmenite [107, 174, 11], hematite [175, 176, 177, 11], biotite [176], olivine [176], pyrolusite [176, 11, 12], limonite, psilomelane, vanadinite, carnotite, cuprite, zincite, brucite, cobaltite, and beryl

[11]. Among these minerals, ilmenite demonstrated excellent mechanical resistance and good thermal properties, while however having a modest oxygen transfer capacity and a tendency to agglomerate.

Few studies have undertaken detailed kinetic modelling to characterize the reaction mechanism. Liu et al. [16] reduced primary (crushed hard rock) preoxidized Canadian ilmenite with CO (10, 20 and 30 %) at 850 °C to 1050 °C in a TGA. A flat grain shrinking core model (R_1 model) characterized their experimental data best with a 1.86 order with respect to gas and an activation energy of 146 kJ mol⁻¹. They derived the model based on the first 40 s at 850 °C, 120 s at 950 °C, and the first 300 s at 1050 °C (initial rates), corresponding to solid conversions of approximately 11 % under 20 %CO on the basis of transferable oxygen. Subsequently, Liu et al. [18] characterized the same experimental data with a shrinking core model (volume shrinking, R_3) with a 2.2 reaction order with respect to the gas phase and an activation energy 170 kJ mol⁻¹.

Abad et al. [17] modeled the oxidation and reduction kinetics of Norwegian concentrated ilmenite with a 2 step changing grain size model (CGSM) with chemical and diffusion dependency in the solid product following the numerical value of the solid conversion. They derived their volumetric shrinking core model (R_3) based on qualitative image analysis and a thermogravimetric analyzer operating between 5 % to 50 % fuel concentrations and various gas product concentrations and between 800 °C to 950 °C. They concluded that reduction rate of ilmenite was first order with respect to reductant partial pressure. The activation energies of pre-oxidized ilmenite were 109, 113 and 170 kJ mol⁻¹ for H₂, CO and CH₄, respectively. The reduction rate decreased with the number of cycles — ageing. After 20 cycles, the gas phase reaction order for CO dropped from 1 to 0.8. The activation energies dropped to 65, 81 and 135 kJ mol⁻¹ for H₂, CO and CH₄, respectively. The activation energies and reaction orders are quite different than those derived by Liu et al. [18], even though both applied the shrinking core model. The origin and composition of the ilmenite (primary versus concentrated secondary ilmenite, from Canada and Norway) might account for some of the difference but it is unlikely to account for either the best fit reaction orders or activation energies. Rather than mineral origin, the large differences in activation energy and reaction order might be due to the model assumptions.

Bao et al. [19] characterized the reduction kinetics of pre-oxidized and foreign ion-promoted Chinese ilmenite (K⁺, Na⁺, and Ca²⁺ at loadings up to 15 %) under 1 % to 11 % CO in a TGA operated at 900 °C. After examining several reaction mechanisms (oxygen ion diffusion from the solid phase reactant-product interface to the surface), they selected the semi-empirical n^{th} order “f(x)” power law to fit their data, while admitting that this approach was only

curve fitting (rather than kinetic modelling). In the case of fresh ilmenite (either preoxidized or ion-promoted), the exponent varied from 0.67 to 2, depending on the foreign ion loading and identity, while that of aged ilmenite varies from 1 (initially preoxidized) to 2 (ion-doped). They concluded in a 0.67 and 1st order power law, leading to R₃ and F₁ models, respectively.

Besides ilmenite, researchers have derived kinetic models for other minerals and supported iron oxides. Abad et al. [92] modelled the reduction of alumina-supported FeO (60 % loading) prepared by freeze granulation. They tested various gas phase compositions including CO/CO₂, H₂/H₂O, as well as CO/H₂ in a pressurized TGA. Considering only shrinking core models (R₁ and R₃), they concluded that the reduction rate was 1st order with respect to CO. The activation energy was only 20 kJ mol⁻¹, suggesting that the reaction rate might be controlled by mass transfer rather than kinetics. Luo et al. [73] modelled the reduction kinetics of Chinese hematite (iron ore) and supported ore. They calculated a 184 kJ mol⁻¹ activation energy for the pure ore using an A₂ model. Monazam et al. [178] modelled the reduction of Canadian hematite by hydrogen following a combination of morphological models to fit the entire range of data. A similar approach was adopted for its reduction under methane in a previous study [75].

The oxidation-reduction kinetics of other metal oxides have been characterized : Ni, Co, Cu, and Mn oxides. Aghabarannejad et al. [179] modeled the oxidation and reduction kinetics of supported Co₃O₄, CuO, and Mn₂O₃ under air and inert atmosphere in the chemical looping with oxygen uncoupling (CLOU) process. They characterized both the reduction and oxidation kinetics using a homogeneous nucleation-growth model (Avrami-Erofeev). In CLOU, the solid is reduced by emitting molecular oxygen, so the choice of the nucleation-growth model is judicious, since it was precisely developed for the homogeneous decomposition of solids [180]. Hossain and de Lasa [147] modelled the reduction of bi-metallic Co-Ni Al₂O₃ supported oxygen carrier under dynamic temperature conditions. They compared the shrinking core and the random nucleation model (a F₁ model), and concluded this model best characterized the kinetics, with an activation energy of 45 kJ mol⁻¹. Iliuta et al. [155] modelled the reduction of Al₂O₃-supported Ni by CH₄ using a combined power law (F₁) and mechanistic approach. The activation energy for the non-catalytic gas-solid reactions ranges from 24 kJ mol⁻¹ to 77 kJ mol⁻¹. Rashidi et al. [76] characterized the reduction of NiO pellets by methane and found a 258 kJ mol⁻¹ activation energy. Maya and Chejne [181] modelled the reduction of supported copper oxide (with CuO loadings ranging from 9 % to 23 %) by considering only the shrinking core model (R₃), with a 50 kJ mol⁻¹ activation energy. Qin et al. [182] modelled the reduction of a mixed Ca-Cu oxide to be used in combined chemical-carbonate looping. They characterized the reduction of CuO by methane using a F₁ power law with a 79 kJ mol⁻¹ activation energy.

Characterization of the reduction kinetics of oxygen carrier by researchers from the Instituto de Carboquímica (Zaragoza, Spain) [92, 183, 184, 185] are generally performed using similar experimental procedure and using the same morphological model (the changing grain size model (CGSM)) : i) The oxygen carrier is reduced (and reoxidized) in a TGA under CH_4 , CO , and H_2 ; ii) the shrinking core model is assumed due to the granular structure of the oxide ; and iii) a hybrid reaction-diffusion limited regime shrinking core model is derived following the extension of the solid conversion. Dueso et al. [185] characterized the reduction kinetics of Ni-based oxygen carriers and calculated activation energies ranging from 5 kJ mol^{-1} to 400 kJ mol^{-1} for NiO and NiO supported on a NiAl_2O_4 spinel. Cabello et al. [183] modelled the oxidation-reduction of Al_2O_3 -supported Fe_2O_3 and estimated activation energies of 66, 8 and 14 kJ mol^{-1} for reduction under CH_4 , H_2 , CO , respectively. Abad et al. [186] and de Diego et al. [184] characterized the kinetics of Ca, Mg, Mn based perovskite by considering the appearance of spherical grains that followed the shrinking core model (R_3), and neglecting external mass transfer resistance for chemical looping with oxygen uncoupling (CLOU) applications. Adanez-Rubio et al. [187] characterized the reduction of CuO to Cu_2O with oxygen generation for CLOU with a hybrid morphological-mechanistic model, relying on a combination of Freundlich isotherm and Avrami-Erofeev model, and calculated a 270 kJ mol^{-1} activation energy. de Diego et al. [184] derived activation energies of 107, 85 and 40 kJ mol^{-1} for reduction under CH_4 , H_2 , CO , respectively. Garcia-Lario et al. [188] model the reduction of Cu oxides using only the shrinking core models (plate-like (R_1/F_0) for small pellets and cylindrical (R_2) for larger ones). They calculated activation energies of 23, 26 and 75 kJ mol^{-1} for reduction under H_2 , CO , and CH_4 , respectively, and almost first order reaction order for the gas.

While there is homogeneity in the modelling approach (power law and shrinking core), great variability results from the characterization of the reduction of ilmenite. Activation energies vary from 81 kJ mol^{-1} to 170 kJ mol^{-1} for the reduction under carbon monoxide, and reaction order for the gas ranges from 0.8 to 2.2. Classical mechanistic models are less common. In order to characterize the kinetics of the reduction of preoxidized ilmenite by methane, we minimize the parameters involved by identifying simpler reaction steps for CO to CO_2 , and H_2 to H_2O . We present here the reduction kinetics of preoxidized ilmenite by carbon monoxide via a mechanistic approach.

4.2 Materials and methods

We preoxidized secondary ilmenite from Richards Bay Minerals (Rio Tinto) in a muffle furnace with a steady flow of air for 24 h at 1000°C . The ilmenite was agglomerated and we

manually crushed it with a pestle and mortar. We recovered the 75 μm to 106 μm diameter particles in a sieve. X-ray crystallography identified the active phases in the fresh and preoxidized mineral : the original ilmenite (containing mostly TiO_2 , FeO and Fe_2O_3 , c.f. Table 4.1) was oxidized to a mixture of ferric pseudobrookite (Fe_2TiO_5), rutile (TiO_2), as well as hematite (Fe_2O_3). Rio Tinto supplied the ilmenite, along with its phase composition certificate. The Scott density of the fresh ilmenite was 2540 kg m^{-3} . An Accupyc 1340 (Micromeritics) gas pycnometer measured the particle density ; it decreased from 4753 kg m^{-3} to 4350 kg m^{-3} after the preoxidation treatment. The measured particle density agree with the theoretical values for ilmenite (4790 kg m^{-3}) and ferric pseudobrookite (4370 kg m^{-3}).

Sieved ilmenite (1 g), and crushed and sieved preoxidized ilmenite (1 g) were loaded to a 7 mm ID quartz reactor equipped with a quartz frit gas distributor inserted at mid-length. The resulting bed height was 1 cm. We inserted a type-K thermocouple in the bed (in contact with the gas distributor) to monitor temperature during the reduction-oxidation runs. An electrical furnace heated the reactor (800°C to 950°C) under a 40 ml min^{-1} (normal conditions) flow of 21 % O_2 in Ar. Ilmenite was sequentially reduced and oxidized by 15, 20 and 25 % CO , and 21 % O_2 , respectively (Figure 4.2). The CO gas cylinder contained 25 % He and the O_2 gas cylinder contained 5 % Kr. He and Kr served as inert tracers for the hydrodynamic modelling of the gas phase. A Hiden QIC-20 quadrupole mass spectrometer monitored CO , CO_2 , and O_2 (the reactants), Kr, He, and the reference and dilution gas, Ar (Figure 4.1).

Based on past experience, the relative sensitivity of the mass spectrometer for a given species is a function of its concentration, but also the presence of other gases being measured, which we accounted for in our calibration of the MS. As a first step, we measured known concentrations of binary mixtures (a compound of interest and the reference gas, e.g. CO in Ar). In this step, we calculated the fractions associated with the ionization of the gas species in the mass spectrometer (e.g. 16 amu fractions associated with the measurement of oxygen). We also determined the relative sensitivity of the mass spectrometer for that compound and used it for reference (to assess the effect of the presence of other species in the case of multicomponent mixtures). As a second step, we measured multicomponent mixtures, knowing the fractions associated with each species. In the case of CO oxidation reactions, we calibrated the mass spectrometer with constant carbon concentrations (sum of CO and CO_2). For a metal oxide reduced with 20 % CO , we calibrated the mass spectrometer with five mixtures of CO and CO_2 always adding to 20 %. Since we reduced ilmenite with 15, 20 and 25 % CO , we calibrated the MS for 15, 20 and 25 % total carbon concentrations, with at least 4 mixtures in every case. The last step consisted of reconciling the gas profiles obtained with the mass balance, closing the mole balance within 3 %.

Tableau 4.1 Composition of the secondary ilmenite from Richards Bay Minerals

Phase	weigh percent
TiO ₂	49.3
FeO	25.0
Fe ₂ O ₃	21.7
MnO	1.3
MgO	0.6
SiO ₂	0.6
Al ₂ O ₃	0.4
V ₂ O ₅	0.3
Cr ₂ O ₃	0.2
CaO	0.1
Na ₂ O	0.1
K ₂ O	0.1
P ₂ O ₅	0.03

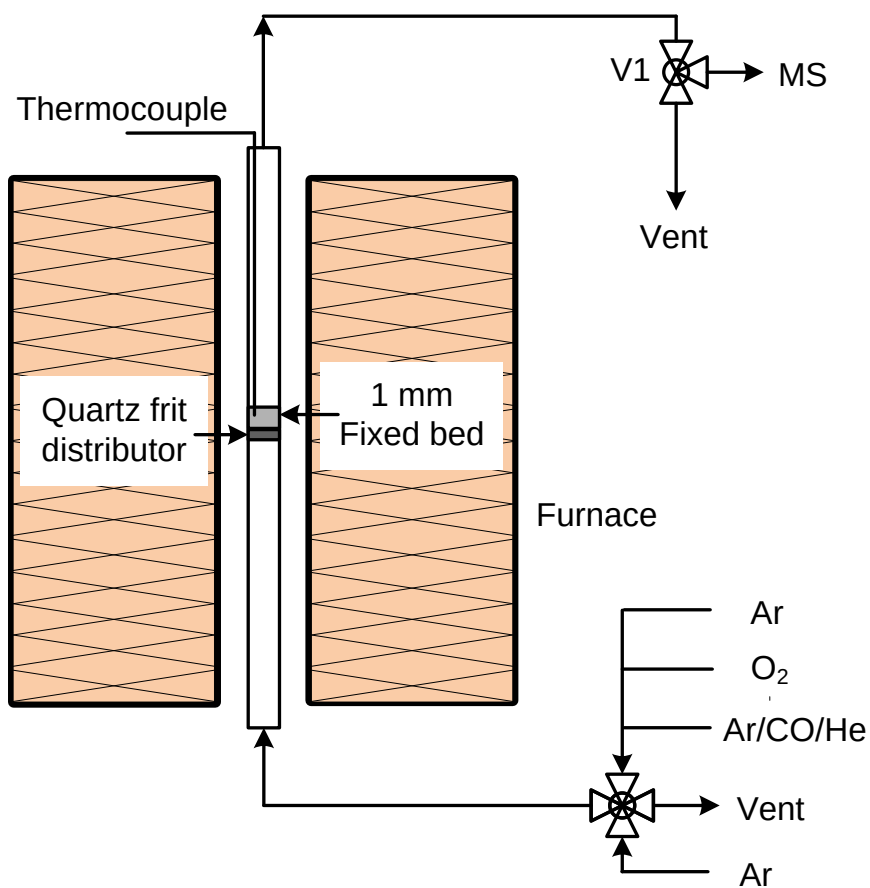


Figure 4.1 Micro-fixed bed experimental set-up for carbon monoxide kinetic experiments

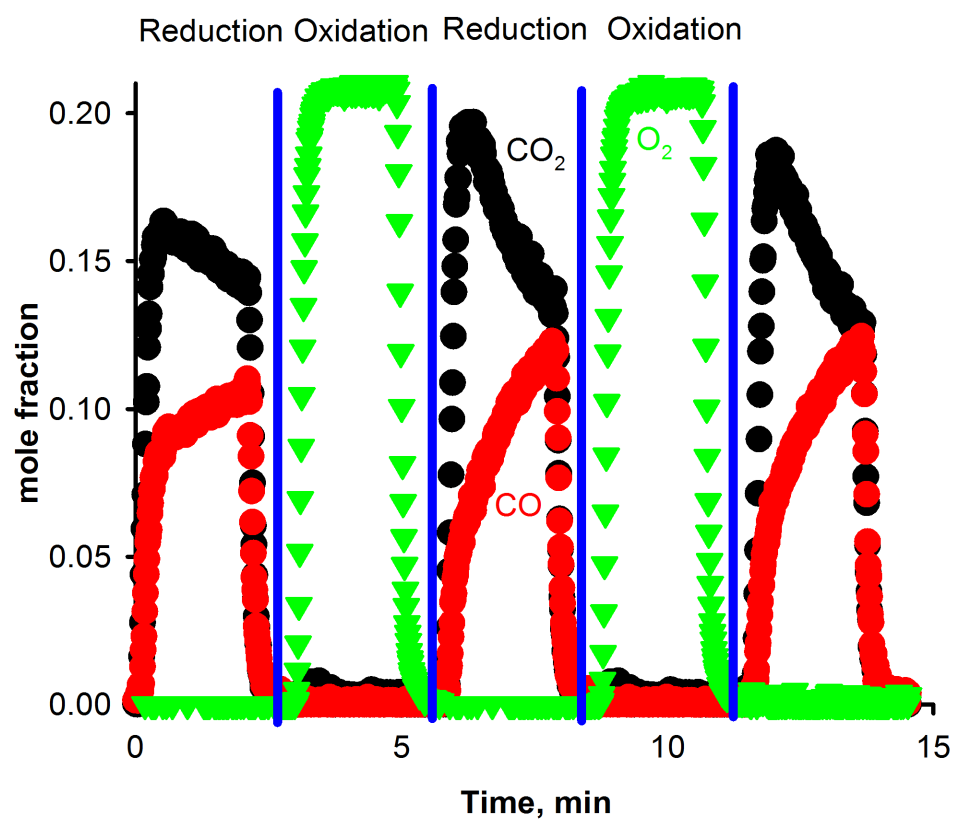


Figure 4.2 Sequential reduction and oxidation of preoxidized ilmenite at 812°C with 25 % CO and 21 % O₂, respectively

We compared the reactivity of fresh and preoxidized ilmenite with CO by sequentially reducing it under 15, 20 and 25 % CO at 800, 850 and 900 °C. We first heated the oxide under a 21 % O₂, bal. Ar between room and reaction temperatures, then switched to pure Ar using an automated 4-way valve to purge the reactor for 5 min. Then, CO was fed to the reactor for 2 min, and switched back to Ar. We finally reoxidized the ilmenite with 21 % O₂ in Ar for 5 min, and purged the reactor with Ar. We repeated the reduction-oxidation cycles three times at each concentration and temperature, for a total of 27 cycles, plus 15 initial cycles oxidized (21 % O₂) and reduced under 15 % H₂ for 5 min at 800 °C. These cycles stabilized ilmenite's chemical reactivity and the data were ignored in the kinetic modelling.

A combined reactor and kinetic model was developed to characterize the reduction of the preoxidized ilmenite with carbon monoxide. We first simulate the hydrodynamics of the gas phase by applying a step change in concentration using a four way valve, and modelled the gas profile measured by the mass spectrometer at the outlet of the reactor. We did so by calculating the axial dispersion coefficient (D_z) of the dispersion model mole balance equation applied to an inert gas tracer (Equation 4.1).

$$\frac{\partial C_{tracer}}{\partial t} = -\frac{\partial(u_z C_{tracer})}{\partial z} + D_z \frac{\partial^2 C_{tracer}}{\partial z^2} \quad (4.1)$$

For CO oxidation reaction (yielding only CO₂ as products), we selected the total carbon in the gas phase (CO plus CO₂) as the ideal hydrodynamic inert tracer. Past experience with inert tracer (e.g. He and Kr) showed that these molecules pass through the reactor and gas analysis section faster (almost pure plug flow). We then used the axial dispersion coefficient in the mole balance equation for each reacting gas phase species.

4.3 Results and discussion

We first compared the mass of oxygen transferred from the solid to the gas phase during reduction of fresh and preoxidized ilmenite, per initial mass of ilmenite and preoxidized ilmenite (Figure 4.3). The specific oxygen transferred when reducing fresh ilmenite with CO was 1.5 times higher than that of preoxidized ilmenite. Fresh ilmenite could transfer up to 1,7 % oxygen on a mass basis, while preoxidized ilmenite have limited capacity (1,2 %). The oxygen transfer increases linearly with the CO concentration. For a given CO concentration, the effect of the temperature on the oxygen transferred is very low. Reducing fresh ilmenite with 15 % CO consumes 1,00 % oxygen on a mass basis, $\pm 0,01$ % (maximum and minimum of a range of measurements) irrespective of the temperature. For reduction under 20 % CO, the oxygen transferred is 1,33 % $\pm 0,01$ % at 809 °C, and peaks at 1,36 % $\pm 0,02$ % at 908 °C.

Finally, when fresh ilmenite was reduced with 25 % CO, $1,64 \% \pm 0,01 \%$ of the mass of the oxide was lost as oxygen into the gas phase at 809°C , and this value reached $1,69 \% \pm 0,02 \%$ at 908°C . For preoxidized ilmenite, the effect of the temperature was more perceptible, even though the oxygen transferred per mass of solid was less than for fresh ilmenite. When reduced with 15 % CO, the oxygen transferred went from 0,6 % to 0,7 % from 820°C to 917°C , 0,88 % to 0,94 % under 20 % CO, 1,13 % to 1,19 % when reduced by 25 % CO. This slight increase in oxygen transferred from 820°C to 917°C for preoxidized ilmenite guarantees a non-zero activation energy if an appropriate kinetic model is selected. Interestingly, even though the oxygen transfer was higher for the fresh ilmenite, when vacating the ilmenite at the end of the experiment, some was agglomerated. This implies that channeling of the gas via preferred path minimized the contact between the gas and the solid. The reported oxygen transfer capacity is underestimated.

To determine the kinetics of the reduction of preoxidized ilmenite under CO, we solved the mole balance applied to a plug flow model with dispersion (Equation 4.2). The reaction rate expressions were obtained by applying the mass action law to elementary reaction steps. The kinetic constants were determined by minimizing the sum of squared residuals using MATLAB's "lsqcurvefit" function, and by calling the partial differential equations solver "pdepe".

$$\frac{\partial C_{i,gas}}{\partial t} = -\frac{\partial(u_z C_{i,gas})}{\partial z} + D_z \frac{\partial^2 C_{i,gas}}{\partial z^2} + \frac{(1-\epsilon)}{\epsilon} \left(\sum_j r_{i,j} \right) \quad (4.2)$$

Of the various reaction rate expressions tested, only one fit the experimental gas phase profiles adequately. The model assumes carbon monoxide reacts with surface oxygen atoms, and bulk lattice oxygen replenishes the surface sites (Figure 4.4). The crystal structure of ilmenite is such that Fe^{2+} and Ti^{4+} occupy alternate layers. We suppose that the oxygen atoms bound to the titanium cation are less reactive but allow oxygen to diffuse. However, due to this alternate crystal structure, a mass transfer resistance could arise.

The chemical and quasi-chemical (*i.e.* involving defects) reactions of the proposed mechanism (Equations 6.7 and 6.8) involve the distinction between surface (O_*) and bulk (O_O) oxygen concentrations. In order to express their corresponding concentration terms in the reaction rate expressions (Equations 6.9 and 6.10), we define N_s (in mol m^{-2}) and N_r (in mol m^{-3}) as the oxygen surface site density and bulk oxygen concentrations, respectively. To model the evolution of the surface and bulk concentrations, we multiply the surface site density and bulk oxygen concentration by surface coverage and normalized bulk oxygen concentrations, θ_{O*} and γ_{Ob} , respectively.

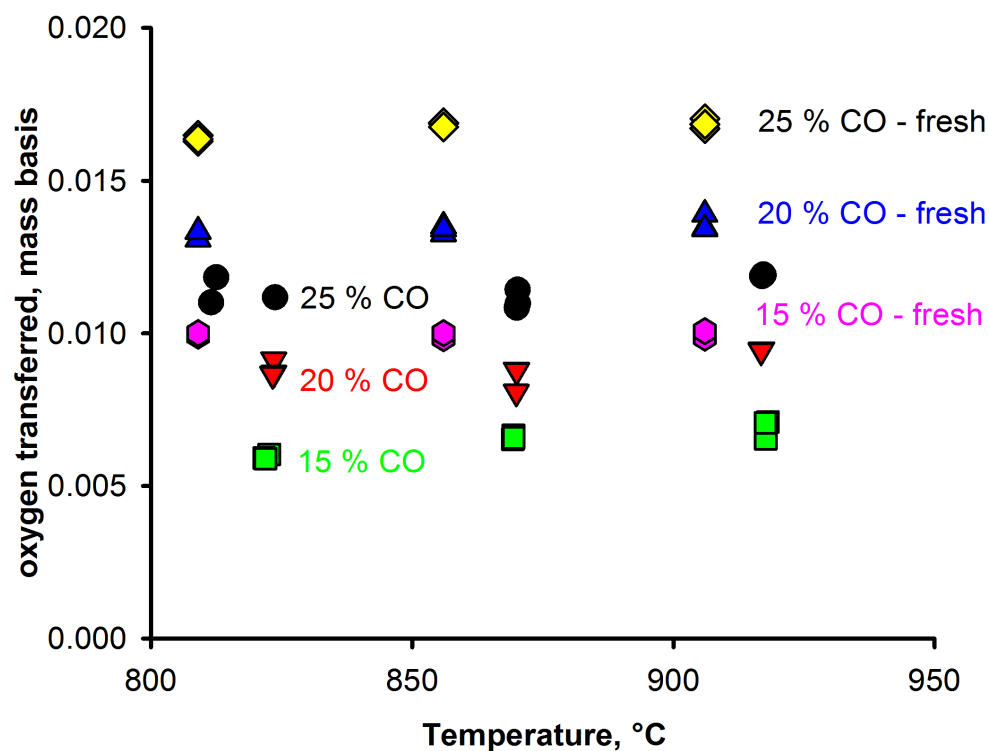


Figure 4.3 Squares : Preoxidized ilmenite reduced with 15 % CO ; Down triangles : Preoxidized ilmenite reduced with 20 % CO ; Circles : Preoxidized ilmenite reduced with 25 % CO ; Hexagons : Fresh ilmenite reduced with 15 % CO ; Up triangles : Fresh ilmenite reduced with 20 % CO ; Diamond : Fresh ilmenite reduced with 25 % CO.



$$r_1 = k'_1 P y_{\text{CO}} N_s \theta_{\text{O}^*}$$
(4.5)

$$r_2 = k'_2 N_s (1 - \theta_{\text{O}^*}) N_r \gamma_{\text{O}_b}$$
(4.6)

While the surface site density was taken as a parameter in the curve fitting procedure, the bulk oxygen concentration term was estimated using the theoretical oxygen transfer capacity concept, a mass ratio of the removable oxygen to total mass of the oxide. For ferric pseudobrookite, the theoretical oxygen transfer capacity is 5 %. The bulk oxygen concentration is then expressed as the product of the bulk density ρ_b and the theoretical oxygen transfer capacity $R_{\text{O},th}$, divided by the oxygen molar mass M_{O} (Equation 4.7).

$$N_r = \frac{\rho_b R_{\text{O},th}}{M_{\text{O}}}$$
(4.7)

Arrhenius plots of the 24 experiments indicated the the activation energy of the gas-surface reaction was close to zero. The first reduction cycles after an extended contact with an oxygen rich atmosphere were discarded from the kinetic modelling : the oxygen transfer capacities were larger possibly due to weakly bonded molecular oxygen. According to Vannice [189], a zero activation energy can be caused by the presence of external mass transfer limitation (diffusion of the gaseous reactant from the bulk to the surface and/or of the gas phase product in the opposite direction). We tested this hypothesis by adding a gas phase mass transfer limitation, and modified the mole balance equations to include bulk and surface gas phase species (Equations 4.8 and 4.9). The reaction rate expression for the surface reaction was modified accordingly (Equation 4.10).

$$\frac{\partial C_{i,gas}}{\partial t} = -\frac{\partial(u_z C_{i,gas})}{\partial z} + D_z \frac{\partial^2 C_{i,gas}}{\partial z^2} + \frac{(1-\epsilon)}{\epsilon} k_g a (C_{i,gas}^{(s)} - C_{i,gas})$$
(4.8)

$$\frac{\partial C_{i,gas}^{(s)}}{\partial t} = k_g a (C_{i,gas} - C_{i,gas}^{(s)}) + \sum_j r_{i,j}$$
(4.9)

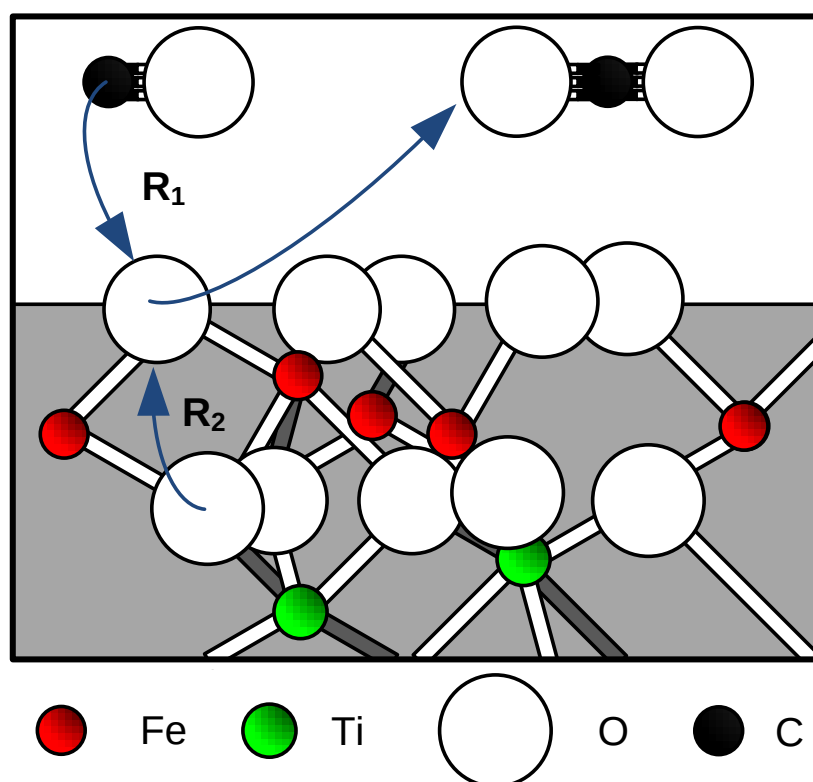


Figure 4.4 CO reduces preoxidized ilmenite. Oxygen atoms from the lattice replenish the surface sites.

$$r_1 = k'_1 P y_{CO}^{(s)} N_s \theta_{O*} \quad (4.10)$$

Adding external mass transfer resistance adds complexity since 2 additional mole balance have to be solved. In turn, the reaction rate for the surface reaction is now a function of the surface CO concentration. The surface CO concentration being lower than that of the bulk (Figure 4.5), the kinetic constant of the surface reaction is now higher compared to the model without external mass transfer limitations.

The resulting model accounts for more than 90 % of the variance of the experimental gas profiles (Figure 4.6), and the activation energy of the surface reaction is no longer zero. Its value is 50 kJ mol^{-1} and that of the bulk to surface reoxidation reaction is 90 kJ mol^{-1} . CO is converted to CO_2 as soon as it is fed, and carbon dioxide reaches a peak after 25 s. After reaching a maximum, the CO_2 concentration decreases slightly and approaches a constant value for the last 30 s. This apparent equilibrium between CO and CO_2 is transitory, and the ratio changes for longer reaction times.

The surface oxygen replenishment step in our kinetic mechanism is similar to the prevailing models describing the oxygen diffusion through the oxide-ion conducting electrolyte of solid oxide fuel cells : once molecular oxygen is reduced ($\text{O}_2 \rightarrow \text{O}^{2-}$), the oxygen ions must diffuse through the oxygen sublattice of the oxide. This diffusion process leaves behind oxygen vacancies. This mechanism can also be analyzed in terms of charge neutrality : the oxygen vacancies diffuses from the surface to the center of the particles. Positively charged ferric or ferrous cations could also be involved and build up towards the center of the particles due to their migration in the opposite direction of the oxygen ions to maintain charge neutrality. Cations that accumulate topochemically could be incorrectly interpreted as a reaction front like a shrinking core.

Among the 140 articles discussing ilmenite, three characterized the reaction kinetics with a shrinking core model [17, 16, 18]. All reaction steps are lumped together as a single parameter [190]; activation energies range from 81 kJ mol^{-1} to 170 kJ mol^{-1} and gas phase reaction orders from 0.67 to 2. We tested this model and several other morphological models by deconvoluting the gas phase profiles to compute the solid conversion. The shrinking core and power law models account for the variance in the data equally well as our mechanistic model. Neither Abad et al. [17] nor Liu et al. [16, 18] mentioned having tested different models. However, Liu et al. [16, 18] acknowledged the curve fitting nature of their work.

Some authors observed the presence of metallic iron at the grain boundaries after having reduced ilmenite or ferric pseudobrookite (preoxidized ilmenite) with carbon monoxide. Zhao

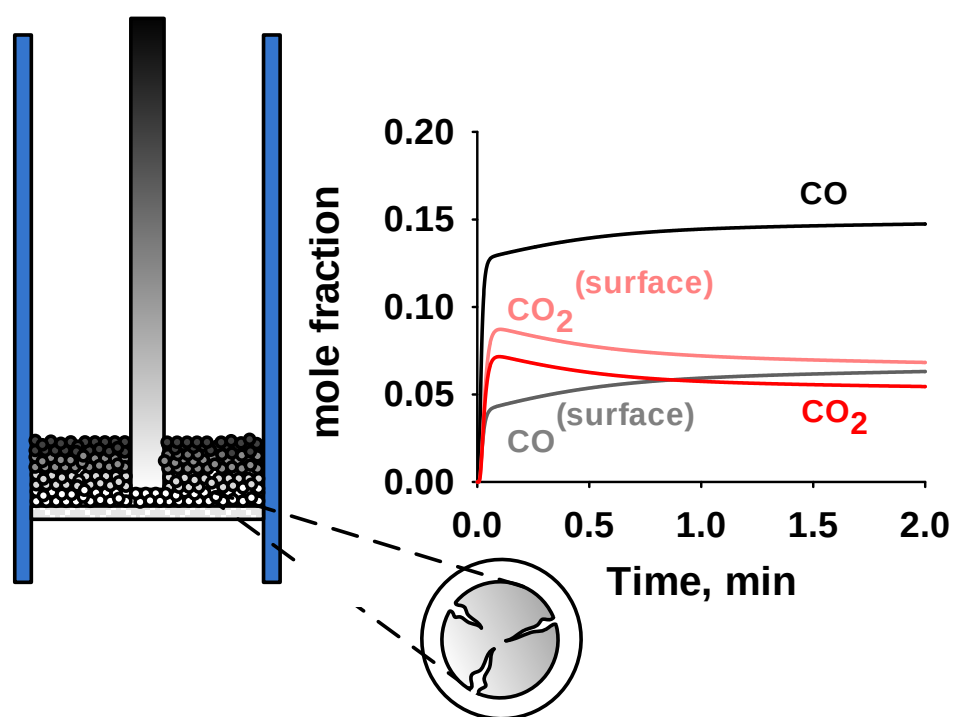


Figure 4.5 The bulk CO concentration is larger than its surface counterpart. The surface CO₂ concentration is higher than the bulk since little CO₂ is produced on particles located below

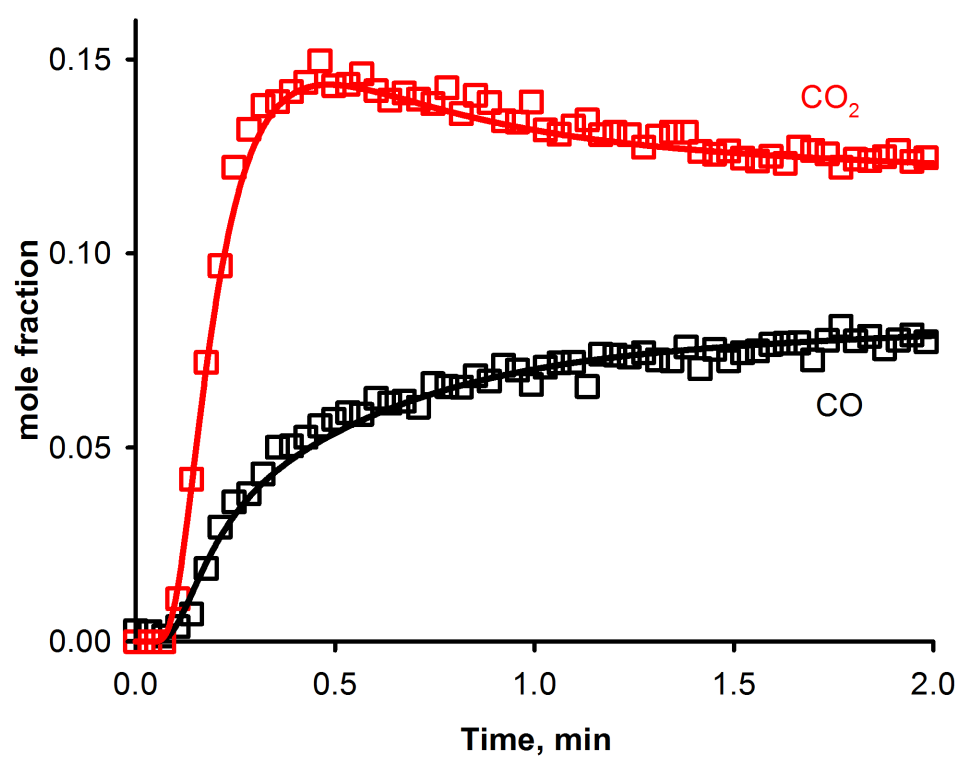


Figure 4.6 The model (solid line) accounts for more than 99 % of the variance in the experimental data (symbols) recorded by the MS.

and Shadman [191] concluded that metallic iron diffuses at the grain boundaries when reducing synthetic ilmenite with CO for more than 90 min. However, Jones [192] reported metallic iron after reducing preoxidized ilmenite with CO only at temperature higher than 1200 °C. In the case of fresh ilmenite, he describes the reaction front as a place where Fe^{2+} is replaced by manganese or magnesium ions, preventing the further reduction of Fe(II). SEM-EDX element mapping of metallographic cuts of reduced particles was inconclusive with respect to the presence of unreacted reaction fronts inside the particles (Figure 4.7). Instead, we observed iron and oxygen-rich regions at the particles boundaries. Titanium was uniformly distributed.

The differences between our model and that of other researchers in CLC can be explained by kinetic model preferences. Abad et al. [17] did not rely on SEM images nor SEM-EDS metallographic cuts for their choice to model the data using one of the shrinking core family models (SCM). They only observed a granular structure. We opted for the oxygen replenishment model for various reasons : i) SEM-EDS metallographic cuts did not reveal a structure characteristic of unreacted shrinking core, ii) Any of the F_i or R_i morphological models could equally fit the data (illustrating their curve fitting nature), iii) The oxygen replenishment model was the only mechanistic model to fit the data, and iv) Doremus [193] pointed out the lack of experimental data on the diffusion of carbon monoxide in any solids or melts.

The fitted surface site density decreases over the reduction cycle numbers (Figure 4.8) : it decreases monotonically with the reduction cycles, but also with the decreasing CO concentration for a given temperature. This drop can be characterized by using the simple power law expression (SPLE) [194], applied to the normalized surface site density (Equation 4.11), where k_s is the sintering rate constant, n the sintering order, and $N_{s,0}$ the initial surface site density. The best fit for the surface site density is a zero-order (constant derivative) with an activation energy of 67 kJ mol⁻¹.

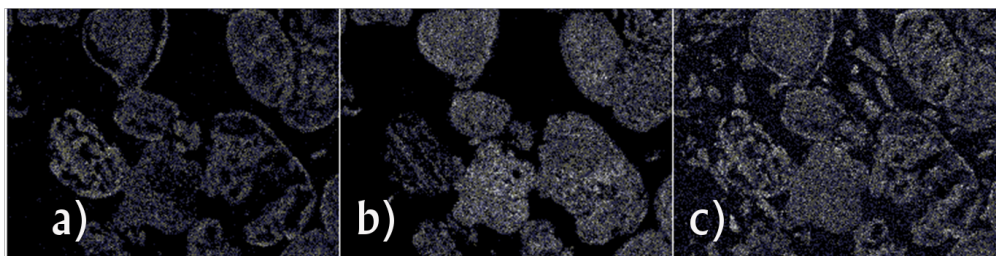


Figure 4.7 EDS mapping of iron (a), titanium (b) and oxygen (c), respectively.

$$-\frac{d(N_s/N_{s,0})}{dt} = k_s(N_s/N_{s,0})^n \quad (4.11)$$

These comments on the agglomeration kinetics of ilmenite are exploratory and consist of a sintering model taken from the kinetic model. However, they correctly qualitatively predict the very important fact that ilmenite (preoxidized or not) is prone to agglomeration. At the end of the kinetic experiments, small agglomerate formed. If ilmenite is to be a serious candidate as an oxygen carrier candidate, a detailed agglomeration programme must be undertaken.

4.4 Conclusion

The recent plunge of the CO₂ trading price has dampened the enthusiasm of industrial partners funding chemical looping technology development and research activities. The trading price may eventually rise again to arouse the interest, and with it, corporate interest. The perfect oxygen carrier must be inexpensive, resistant to attrition and non-toxic. Ilmenite is an interesting oxygen carrier. However, it has a modest oxygen transfer capacity, it is prone to agglomerate, and more importantly, already occupies the economically important TiO₂ production niche market. For chemical looping with natural gas, the kinetics of the reduction of ilmenite by methane must be characterized. As a first step, we modelled its reduction with carbon monoxide via a two step mechanism. The first step involves the reduction of the surface oxidized sites by carbon monoxide molecules. Then, oxygen atoms from the lattice diffuse and reoxidize the reduced surface sites. The reactivity of ilmenite towards CO is such that the reaction is limited by external mass transfer. In addition, the model predicts that the powder gradually sinters.

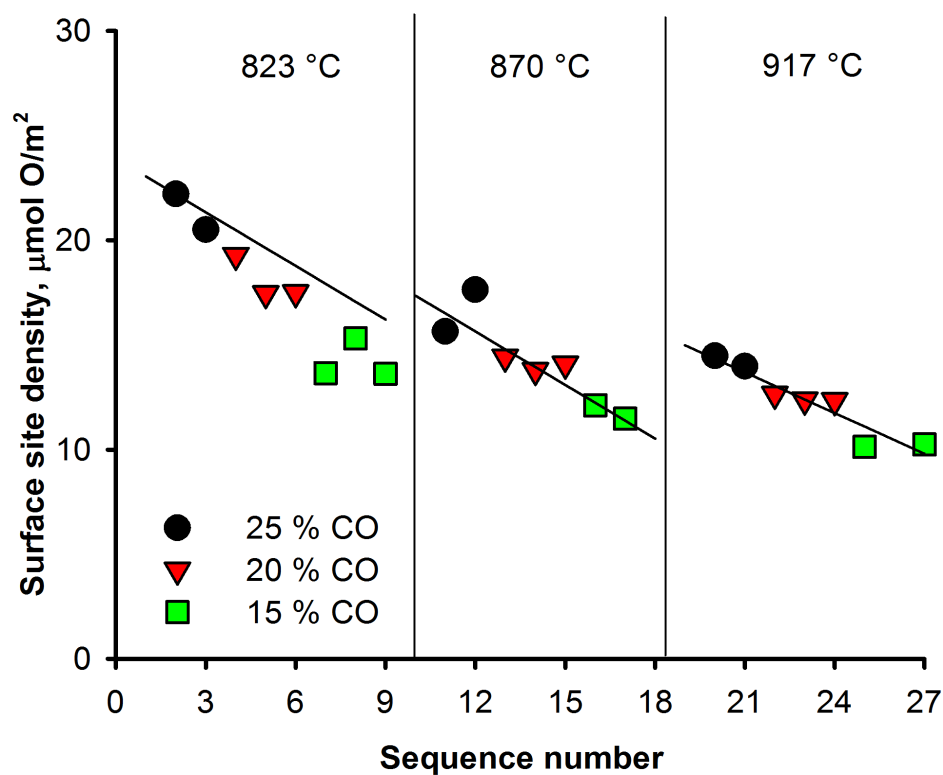


Figure 4.8 The fitted surface site density is monotonically decreasing with the reduction cycle numbers. The decreasing trend can be modeled by the simple power law expression (SPLE) for catalyst deactivation by sintering (solid line).

CHAPITRE 5 ARTICLE 2 : PYROLUSITE–CO REDUCTION KINETICS

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Article publié dans la revue *Chemical Engineering Journal* [173]

Abstract

Pyrolusite is an inexpensive and nontoxic manganese ore with exceptional oxygen transfer capacity that makes it a potential candidate for chemical looping combustion. We evaluate the oxygen transfer capacity and kinetics of pyrolusite, an inexpensive and nontoxic manganese ore. We reduced it with carbon monoxide and a combination of carbon monoxide, methane and hydrogen. At 960 °C, carbon monoxide and hydrogen reduce the calcined pyrolusite 86 % more than does a pure CO stream. We derived a mechanistic kinetic model based on the effluent species concentration during reduction with a combination of methane, carbon monoxide and hydrogen from 810 °C to 960 °C. The direct reduction of surface oxygen sites by carbon monoxide, in equilibrium with the reverse CO₂ reoxidation, in addition to the reoxidation of the surface by oxygen atoms from the bulk of the lattice, explains more than 95 % of the variance of the data. We estimated surface parameters by comparing the carbon monoxide and helium washout curves and by analyzing the initial response to a step change in the inlet concentration. Adsorbed CO increased with temperature, up to 910 °C, where it peaked at 55 μmol m⁻², corresponding to a 70 % covered surface. The estimated oxygen surface site density followed an asymptote at 40 μmol m⁻², in agreement with measured values.

5.1 Introduction

The early concepts of chemical looping evolved in diverse applications. From the initial oxy-combustion process for natural gas [195, 196], solid fuels could be handled with the outbreak of Scott et al. [197]. The process was later reoriented from its initial energy-oriented goal to focus on hydrogen production via chemical looping gasification [79], reforming of coked oxygen carriers [63] or methane [62] and water splitting [59, 60, 64]. Recently, Abanades et al. [28], Manovic and Anthony [29] reformed methane for hydrogen generation with in situ carbon dioxide sequestration by integrating calcium looping cycles with chemical looping (CLC-CaL). In this combined process, the heat generated during the reduction of copper

oxide decomposes calcium carbonate into lime for repeated CO_2 sorption.

In the context of current low CO_2 trading prices, minimizing the cost of oxygen carriers is critical. One way to do so is to identify oxygen carriers of mineral origin, requiring no or minimal pretreatment : Mn-Fe minerals with oxygen uncoupling for solid fuels and high methane conversion [131], cement decorated copper ores to minimize their natural agglomeration tendency [198], hematite for methane [199, 74] or sewage sludge combustion [200], K_2CO_3 -added hematite for direct carbon combustion [201].

Manganese is one of the most abundant elements in the Earth's crust, and pyrolusite is its most important ore. Synthetic manganese oxides have been reported for its oxygen uncoupling properties [186, 78, 202]. However, pyrolusite was tested by Leion et al. [203] as early as 2009, but rejected due to its low crushing strength. Linderholm et al. [139] measured an increase in the petcoke gasification rate, compared to that of ilmenite, and attributed this to the presence of alkali metals naturally present on the manganese ore. Since then, it has been disregarded as a potential oxygen carrier, at least in its pure form, but the addition of iron and calcium oxides improve its mechanical resistance [204, 205, 139]. During calcination, pyrolusite, initially in the form of amorphous MnO_2 , decomposes into bixbyite (Mn_2O_3), hausmannite (Mn_3O_4), and manganosite (MnO). The prevalence of any specific phases depends on the oxygen partial pressure. Kononov et al. [206] measured Mn_2O_3 and Mn_3O_4 when heating pyrolusite under air at 1000°C , but only MnO_2 and Mn_3O_4 under argon. This last result is surprising when considering that pyrolusite (MnO_2) decomposes at 535°C into a mixture of bixbyite, hausmannite, manganosite and molecular oxygen [207].

Pyrolusite is an ideal oxygen carrier. Indeed, various patents involving pyrolusite were filed [138, 208, 34], all of which were the result of the work initiated at Polytechnique Montreal as part of a research contract with Total. Manganese oxides are active catalysts for the combustion of organic compounds, including methane, carbon monoxide, C_3s and VOCs [209, 20]. South African and Australian manganese ore loss up to 20 % of their initial mass when reduced with hydrogen at 1000°C : Pyrolusite forms MnO . The iron oxide, naturally present with manganese minerals, converts to metallic iron [206]. Reducing the surface of a manganese oxide increases its basicity, and decreases its surface site density (less oxygen sites) [210]. In addition, the reduction creates new mineralogical phases (e.g. reduction from MnO_2 to Mn_2O_3), which in turns swells the lattice, by further lowering the number of oxide sites (increased spacing) [210]. The increasing extent of reduction also decreases the Mn-O bond strength, due to the gradual replacement of Mn^{4+} with the larger Mn^{3+} cation [210]. The sole adsorption of CO also modifies the Mn-O bond energy [211]. The reduction of manganese oxide can thus be regarded as autocatalytic. Manganese oxides in the presence of excess

oxygen completely oxidize propane. Adding alumina rich manganese oxide is detrimental : propane now forms CO and propene at the same conditions [209]. In addition, even in the absence of molecular gas-phase oxygen, pure unsupported manganese oxide reduces methane without coking [20], a highly desired property for chemical looping applications (no carbon dioxide in the air reactor).

Aside from its redox properties, pyrolusite can also split CO_2 into CO at high temperature due to the naturally occurring alkali promoters present with the manganese oxide phase. Imbihl and Demuth [212] postulated that CO_2 is activated into CO_2^- over potassium promoters, then dissociates into CO and atomic surface oxygen, which rapidly integrates into the lattice. Finocchio and Busca [209] observed a strong IR peak at 2338 cm^{-1} when heating Mn_3O_4 in air at 400°C , followed by vacuum. They associated this peak with trapped CO_2 (in addition to the observed carbonate bands).

In this article, we characterize the kinetics of the reduction of pyrolusite by CO, as well as how much oxygen transfers from the solid to the gas when both CO and H_2 are fed over the catalyst. We derive elementary steps based on the gas profiles from syngas reduction experiments, as well as with a combination of methane and carbon monoxide from 810°C to 960°C . We propose a method to estimate two surface reaction characteristics : surface site density and amount of adsorbed CO. Both parameters are obtained from the transient response with a step change in the inlet concentration.

5.2 Material and methods

We sourced pyrolusite from Centra Africa (via Total SA France) and sieved it to recover the $90\text{ }\mu\text{m}$ to $106\text{ }\mu\text{m}$ diameter particles. Beside MnO_2 , pyrolusite contains mostly iron oxides, alumina, silica and potassium, as measured by X-ray fluorescence performed at the UQAM's Research Center NanoQAM (Table 6.2). The bulk density was $1,78\text{ g cm}^{-3}$ (Scott volumeter) and the particle density was $4,28\text{ g cm}^{-3}$ (Micromeritics Accupyc 1340 gas pycnometer). The fresh pyrolusite, initially amorphous following XRD measurements, has a $7,3\text{ m}^2\text{ g}^{-1}$ specific surface area (Quantachrome Autosorb-1 gas sorption analyzer).

We loaded $0,06\text{ g}$ to $0,1\text{ g}$ to a 7 mmID quartz reactor with a quartz frit gas distributor. An electrical furnace heated the reactor (800°C to 950°C) under an upward steady flow of gas consisting of 21 vol. % O_2 in Ar. Upon reaching the desired temperature, various reductants (CO , H_2 and CH_4 in Ar) and combinations reduced the sample and oxygen in Ar reoxidized it. We sequentially reduced and oxidized the sample with H_2 and O_2 15 times at 800°C before using the data for kinetic modeling, followed by kinetic runs with H_2 , CO, CH_4 , com-

bined reduction (CO/H_2 , CH_4/H_2 , CH_4/CO), as well as CO_2 and H_2O splitting. The design of experiments included minimally 3 concentrations for both the reductants and oxidants, 4 temperatures (800–950 °C), with two repeats at each condition. As a consequence of this programme, the same oxide sample was sequentially oxidized and reduced 303 times. In the case of carbon monoxide reduction, we varied the concentration in the 5-25 vol. % range. For the combined CO/H_2 tests, we varied the CO concentration between 15 and 25 vol. %, and that of hydrogen between 12 and 20 vol. % (by diluting the 25 vol. % CO – 20 vol. % H_2 gas cylinder with Ar). The streams switched between reducing and oxidizing (with inert purge of Ar in between) with a four-way valve to generate step changes in the inlet concentration (Fig. 5.1). Massflow controllers metered the gas at 50 mL min^{-1} (NTP), resulting in a 2.2 cm s^{-1} superficial gas velocity, i.e. lower than pyrolusite’s minimum fluidizing velocity. A Hiden QIC-20 quadrupole mass spectrometer monitored the gas product concentration (m/Z of 2, 16, 18, 28, 40, and 44 amu) at a 1,2 Hz frequency.

We operated the reactor in a fixed bed mode and modeled the hydrodynamics as a tubular flow reactor with axial dispersion and the feed lines as plug flow. We estimated the dispersion coefficient of the inlet lines from the 4-way valve to the reactor by introducing a step change in the inlet gas composition from Ar to $\text{CO} + \text{He}$ and modeled the response of the MS signal at the outlet. The fitted axial dispersion coefficient was $1.9 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$, i.e. equivalent to 36 CSTRs in series, which is essentially plug flow.

We calculated the experimental oxygen transfer capacity by considering the total CO_2 emitted during the reduction by CO (mole balance on transferred oxygen, i.e. Eq. 5.1).

$$R_{O,exp} = \frac{P\dot{V}}{RT} \int_{t_{red0}}^{t_{redf}} y_{\text{CO}_2} dt \quad (5.1)$$

5.3 Results and discussion

5.3.1 Oxygen transfer capacity

The oxygen transfer capacity of pyrolusite reduced with CO reaches an asymptote (Fig. 5.2). It peaked at 2 % on a mass basis (mass of oxygen transferred per initial mass of pyrolusite) for 2 min reductions. An increase in temperature is slightly detrimental : The oxygen transferred from 808 °C to 958 °C decreases by 18 %. Increasing the CO concentration does not increase the oxygen transfer capacity beyond the asymptotic value. We hypothesized that increasing the CO concentration over a threshold value saturates or sterically overcrowds the surface, thus having no net effect on the surface reaction rate and oxygen transfer. Similarly, Feng et al. [213] observed that during the reduction of CO_2 on Sm-doped CeO_{2-x} , the surface

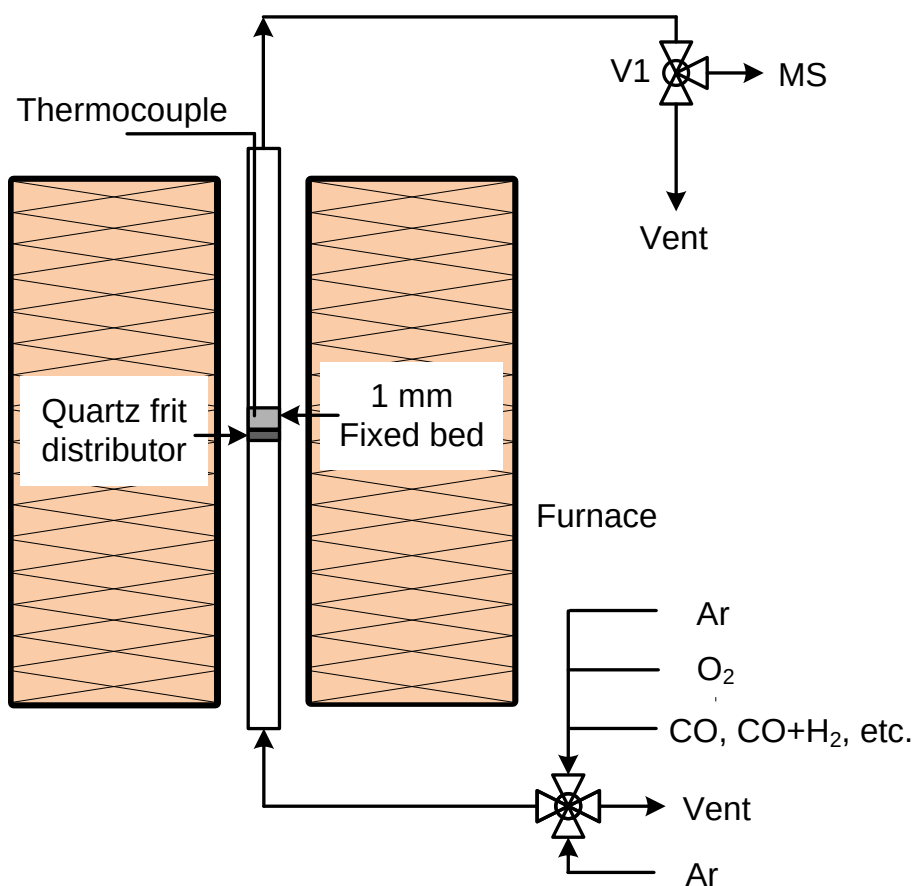


Figure 5.1 Argon purges the reactor after each oxidation and reduction step.

Tableau 5.1 Elemental composition of fresh pyrolusite as measured by X-ray fluorescence.

[The sample also contains Ca, P, Zn, Cu, Mg, Na, S, Cr and S levels below 0,1 %.]

Element	weigh percent
Mn	62.40
O	26.46
Fe	4.06
Al	3.32
Si	1.62
K	0.81
Ba	0.48
Ni	0.17
Co	0.13
Ti	0.10

becomes quickly saturated with carbonates, limiting the further electroreduction of CO_2 at 500°C . They attributed the saturation to an increase of the CO_2 adsorption enthalpy when the coverage approached $1/3$, due to interactions between carbonate species, based on first principles simulation [214].

On the contrary, reducing calcined pyrolusite with a combination of CO and H_2 ($\text{CO}:\text{H}_2$ ratio of 5:4) increases the oxygen transfer capacity. Considering only the oxygen coming from the CO_2 emitted (excluding the water in the oxygen mole balance), we measured a 50% increase at 810°C when compared to that of pyrolusite reduced by CO . At 960°C , the oxygen transfer increases by as much as 86% when reducing with 20 vol. % CO , and doubles when reducing with 25 vol. % CO . We see an almost linear trend between the 5 and 10 vol. % reduction with CO only, and the higher CO concentrations with combined CO and H_2 . Assuming that the reduction by CO is limited by steric overcrowding and so limited by oxygen diffusion from the bulk to the surface fueling the surface reaction, reduction by hydrogen enhances the oxygen diffusion. Diffusion jumps are mediated by lattice defects such as vacancies, following the random walk theory [215]. Hydrogen facilitates diffusion by increasing the number of vacancies, but not only in absolute number, but by increasing it further into the solid crystal structure. Hydrogen permeates through various materials. We suppose that hydrogen removes oxygen both from the surface (O^*) and the crystal lattice (O_O), i.e. via Eq. 5.2 and 5.3. The oxygen transfer capacity approaches an asymptote with increasing CO concentration and temperature in combined CO/H_2 reductions, as was the case of reduction by CO .



5.3.2 CO reduction and CO_2 splitting

A stream of 25 vol. % reduced the calcined pyrolusite, and 25 vol. % CO_2 reoxidized it (the reverse reaction) from 810°C to 960°C . When reducing the calcined pyrolusite, the mass spectrometer measured an instantaneous CO_2 peak as soon as carbon monoxide reached the bed (Fig. 5.3). Following this initial peak, CO_2 gradually decreased and approached a 1,2% concentration, suggesting an equilibrium. This equilibrium was confirmed when splitting CO_2 , as well as when characterizing the kinetics of this reaction. When dosing the reduced pyrolusite with carbon dioxide, after the initial 12% CO peak followed by a slow decreasing

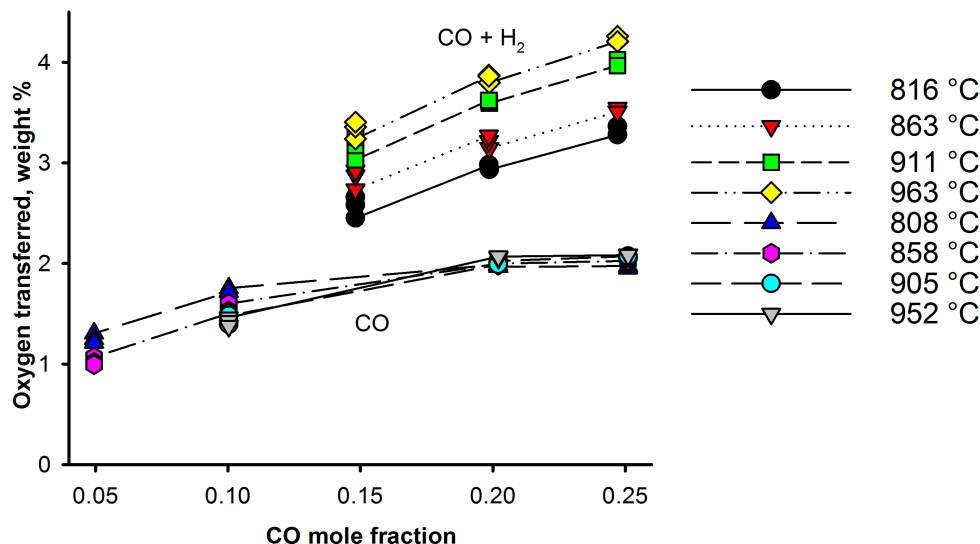


Figure 5.2 The reported oxygen transfer is calculated from a mole balance on the CO_2 measured (coming from the CO only).

concentration, the CO concentration converged to a constant value (1,8%, c.f. Fig. 5.4). To model the CO_2 splitting reaction, we assumed an equilibrium between the forward and reverse reactions to fit the data.

In order to understand the mechanism of CO_2 splitting, we also fed CO_2 over fully oxidized pyrolusite, then fed molecular oxygen at 800 °C. During CO_2 dosing over oxidized pyrolusite, the net result was a deficit in CO_2 , and the MS did not detect other gas phase species. Then, when feeding molecular oxygen, the MS records CO_2 . We excluded coking as the CO_2 sorption process : Reoxidation of a coked catalyst leads to both carbon dioxide and monoxide (not measured). The oxidized form of the calcined cycled pyrolusite cannot split CO_2 , where its reduced state can. We also excluded the formation of surface carbonates in the reaction mechanism based on thermodynamic considerations. Following thermodynamics (HCS 5.0), manganese carbonates form when reducing Mn_2O_3 and Mn_3O_4 with CO at temperatures up to 700 °C. Dosing Mn_2O_3 and Mn_3O_4 with CO_2 forms MnCO_3 up to 400 °C. The XRD diffractograms of fresh sample (amorphous), reduced by CO (MnO), then dosed with CO_2 (still MnO), and finally reoxidized by molecular oxygen (Mn_3O_4) did not match the characteristic peaks of manganese carbonates. Freund and Roberts [216] reviewed the interactions of CO_2 and various metal oxides surfaces, and concluded on the formation of carbonate only at low temperature. We recently showed that the CO_2 splitting reaction was mediated by po-

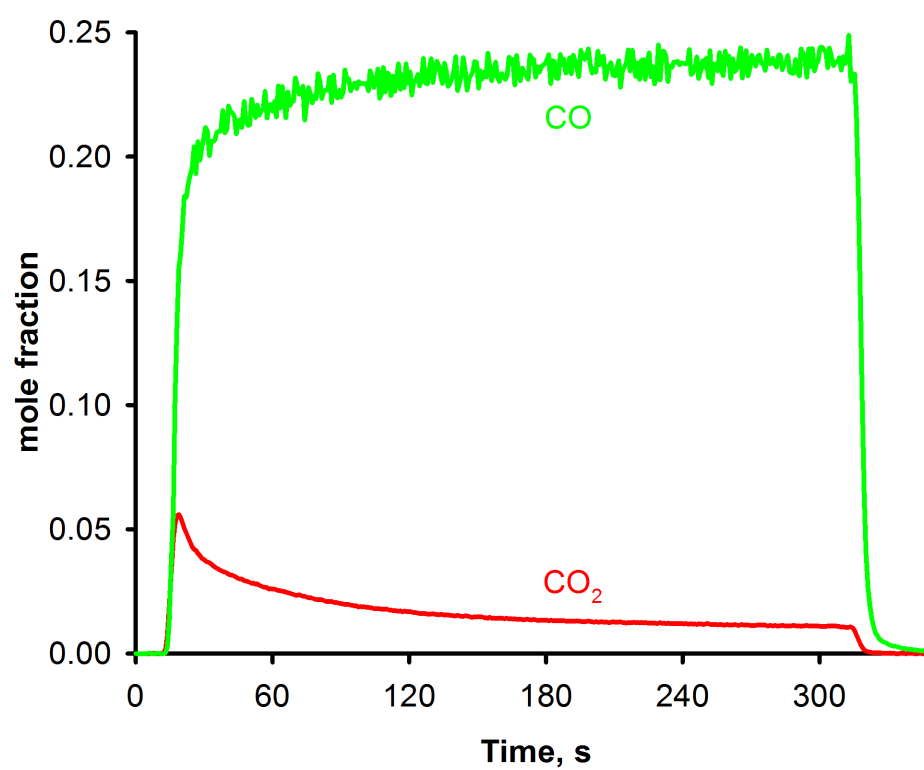


Figure 5.3 Reduction of pyrolusite with 25 % carbon monoxide at 957 °C during alternating CO₂ splitting and reduction by CO.

tassium promoters, activating the inert molecule into a $\text{CO}_2^{\delta-}$ activated state, which further dissociates into CO and atomic oxygen migrating in the bulk of the oxide [69].

5.3.3 Combined CO and H₂ reduction

When reducing calcined pyrolusite with 25 vol. % CO and 20 vol. % H₂ at 817°C, both reactions proceed instantaneously (Fig. 5.5). As soon as the reducing gases reach the bed, the MS records a 15% CO₂ peak, and hydrogen is consumed (water is not plotted in the figures). The initial CO₂ peak is three times greater than that measured during the reduction by 5 vol. % CO, and stays at higher values for most of the reduction. However, after 90 s of reduction, the CO₂ value drops below 2,9% (at 810°C), i.e. lower than the apparent equilibrium CO₂ values for reduction by CO. At 960°C, both the surface reactions and diffusion are faster (Fig. 5.6). In this case, the initial CO₂ concentration is 2.4 that for CO only, and the CO₂ mole fraction stays at higher value compared to when reducing with pure CO (apparent equilibrium at 1,2%). When comparing the gas profiles at 817°C, and 960°C, we observe a greater global extent of reduction (due to CO and H₂) and the MS records a second peak for CO₂. From 817°C to 960°C, the initial CO₂ peak slightly decrease from 15% to 13%, but the H₂ conversion is higher (higher hydrogen consumption highlighted by the gentler slope for the rising hydrogen concentration). There is also a change of slope for all compounds at 65s. We assign the second CO₂ peak to diffusion, i.e. a rapid renewal of the surface oxygen. After CO reduced the surface of the oxide, it is refueled. In that case, the diffusion rate is higher than the surface reaction rate, at least for 15s. Thereafter, the diffusion rate slows : The remaining oxygen lies deeper in the oxide crystal structure. The change in the slope of CO, H₂, and CO₂ may be due to some critical depth upon which diffusion further slows down. This diffusion depth might coincide with a localized change in stoichiometry (appearance of the sufficiently large product grain that induces a discontinuity in the diffusivity). Following this assumption, the faster initial diffusion rate could only be attributed to deviations from stoichiometry, or equivalently, oxygen diffusing from a crystal lattice of distinct nature (lattice sites of different oxide phases, c.f. Eq. 5.4 and Eq. 5.5).



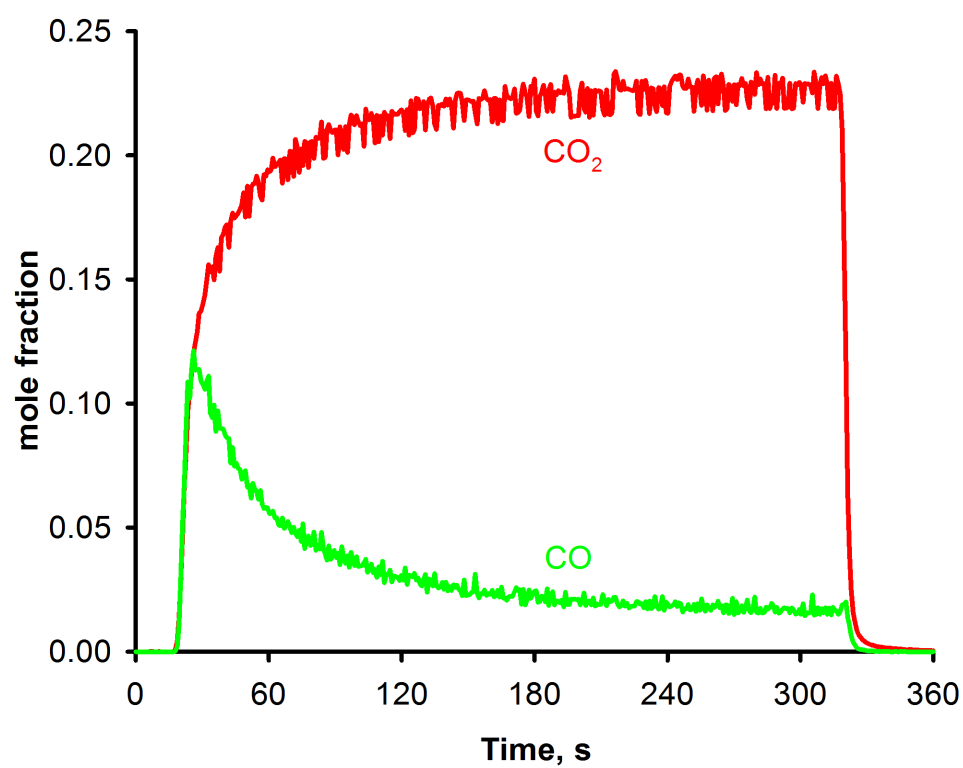


Figure 5.4 Splitting of a 25 % CO_2 stream with reduced pyrolusite at 957 °C.

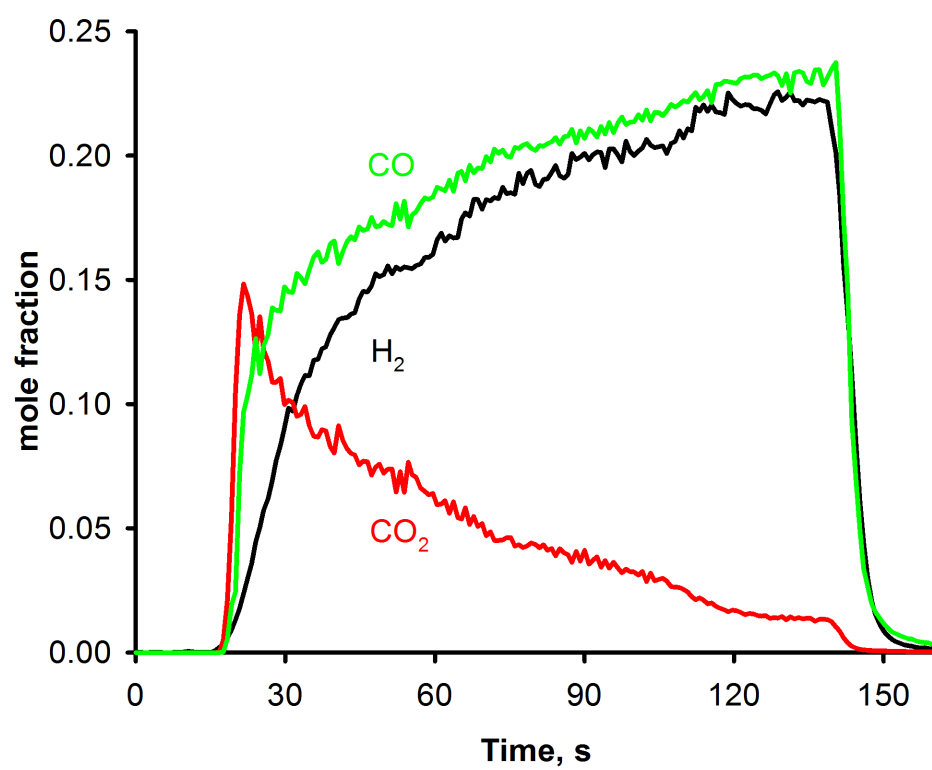


Figure 5.5 Reduction of pyrolusite with 25 % carbon monoxide and 20 % hydrogen at 817 °C.

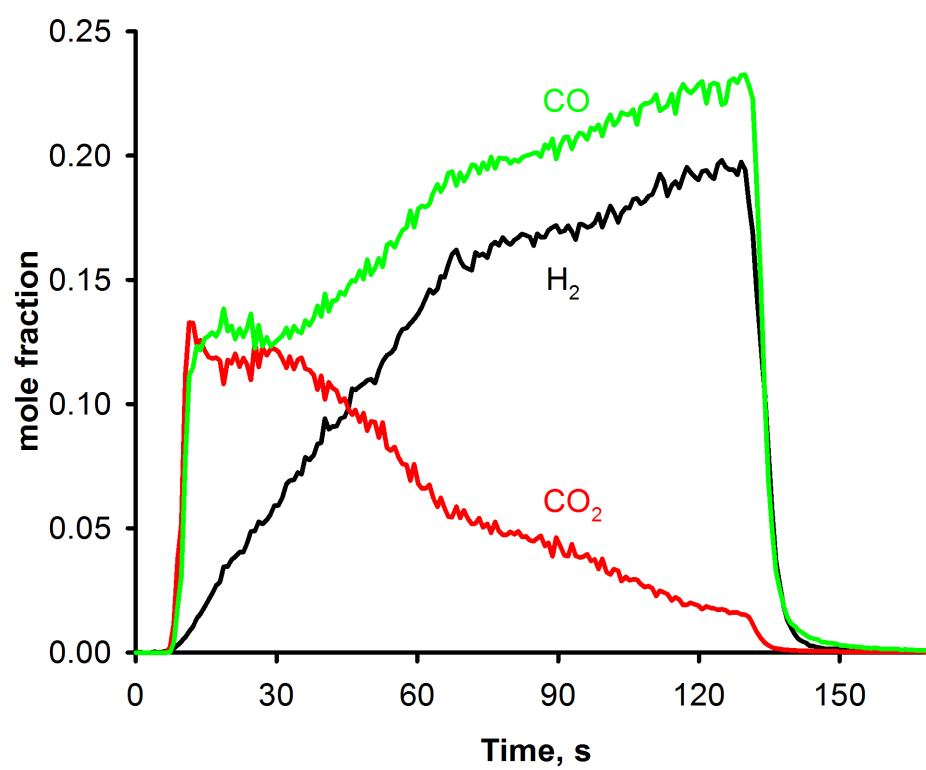


Figure 5.6 Reduction of pyrolusite with 25 % carbon monoxide and 20 % hydrogen at 960 °C.

5.3.4 Combined CH₄ and CO reduction

A combination of 15 vol. % methane and 25 vol. % carbon monoxide also reduced calcined pyrolusite (Fig. 5.7). Pyrolusite first reacts with carbon monoxide to produce carbon dioxide (Eq. 5.6), but methane concentration increases to its inlet value unchanged. Carbon monoxide and methane molecules may compete for the same oxidized sites, with methane being disadvantaged due to steric factors. For the first 5 s of reduction, the methane concentration remains at 15 %, then decreases while the CO gradually increases. The decrease of the methane concentration coincides with an increase in hydrogen, suggesting coking by thermal decomposition of methane (Eq. 5.7). Some of the hydrogen generated reduces the solid producing water (not shown and not quantified due to its distinct hydrodynamic behavior in the analysis section). Methane cokes at a constant rate (almost constant methane concentration after the first 40 s of the reduction). We confirmed coking of the oxide during the reoxidation of the oxide with molecular oxygen (emission of CO and CO₂, then O₂ breaks through). The mass spectrometer detected CO and CO₂, with the total carbon corresponding to 0,4 % of the total carbon fed to the reactor. In addition, when plotting the total carbon concentration (sum of CO, CO₂ and CH₄) against reduction time, the mole balance on carbon diverges with time-on-stream.



Similarly to the combined carbon monoxide and hydrogen reduction, we observed a double peak in CO₂ concentration (Fig. 5.7). The first peak is undoubtedly due to the direct pyrolusite reduction with CO. The second peak may result from the combined effect of the diffusion of oxygen replenishing the surface, as well as the complete combustion of methane over the oxide, most probably via a carbon monoxide formation elementary step. After the induction period, the coverage of surface oxygen decreases, so a one step complete combustion reaction involving methane seems unlikely. The formation of CO would also explain the sharp increase in CO concentration (Eq. 5.8), as well as the slight increase in hydrogen concentration (change in slope at around 30 s for both the hydrogen and carbon monoxide). The location of the pit between the two CO₂ peaks probably indicates the point at which methane converts to CO, but also the initiation of the thermal decomposition of methane. The change in the slope for hydrogen concentration would then be attributed to the addition of the hydrogen resulting from the partial combustion of methane to that due to methane

thermal decomposition via coking.



At 952 °C (Fig. 5.8), the CO combustion rate is doubled compared to that measured at 814 °C. As soon as CO reaches the bed, the carbon monoxide concentration increased to 14 %, then starts to decrease. However, due to the shorter induction time for methane conversion, the second CO₂ peak almost overlaps with the first one. This second peak is now higher and wider than the first one. Methane also partially converts to CO and H₂ at higher rate than at 814 °C (second CO₂ peak due to the CO that further reduces the solid), in agreement with thermodynamic equilibrium composition calculations. At 952 °C, methane cokes 5 times more than it did at 814 °C. However, thermodynamics predicts that coking decreases with temperature.

When switching back to argon after the reduction, carbon monoxide does not fall back to zero instantaneously, or as fast as the other gases, suggesting the presence of adsorbed CO species. Since the direct CO combustion is fast, these species can be attributed to the partial methane conversion reaction (Eq. 5.8), and the desorption that follows (Eq. 5.9).



5.3.5 Kinetic modeling of calcined pyrolusite reduced with carbon monoxide

We characterized the kinetics of the reduction by CO of calcined pyrolusite stabilized over more than 200 oxidation-reduction cycles. The elementary reaction steps were chosen following our previous analysis of gas profiles (Eq. 5.2 to 5.9), for which only reactions 5.5 and 5.6 apply to reduction by CO. We calculated the reaction rates by applying the mass action law (Equations 6.9 and 6.10), and by defining N_s as the oxidized surface site density (in mol m⁻²), θ_{O^*} its coverage, N_r the initial concentration of oxygen in the bulk per volume of bed (in mol m⁻³), and $\gamma_{O,b}$ its normalized concentration.

$$r_1 = k'_1 P y_{\text{CO}} N_s \theta_{O^*} \quad (5.10)$$

$$r_2 = k'_2 N_s (1 - \theta_{O^*}) N_r \gamma_{O,b} \quad (5.11)$$

We assumed a fixed bed with dispersion (Eq. 5.12) based on the results of an inert tracer fed

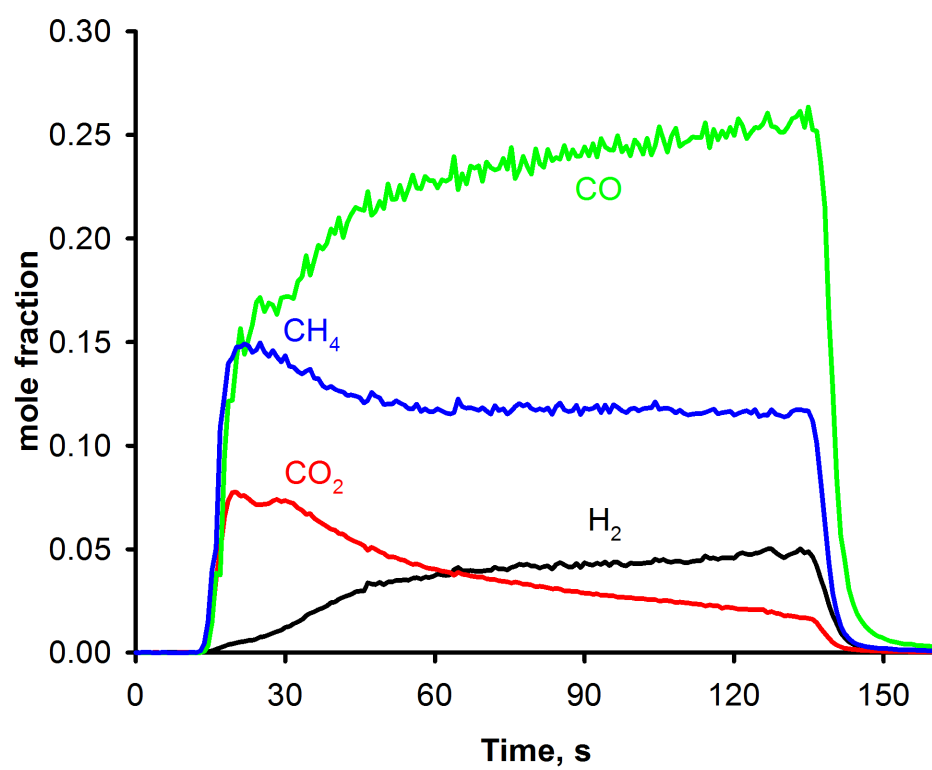


Figure 5.7 Reduction of pyrolusite with 25 % carbon monoxide and 15 % methane at 814 °C.

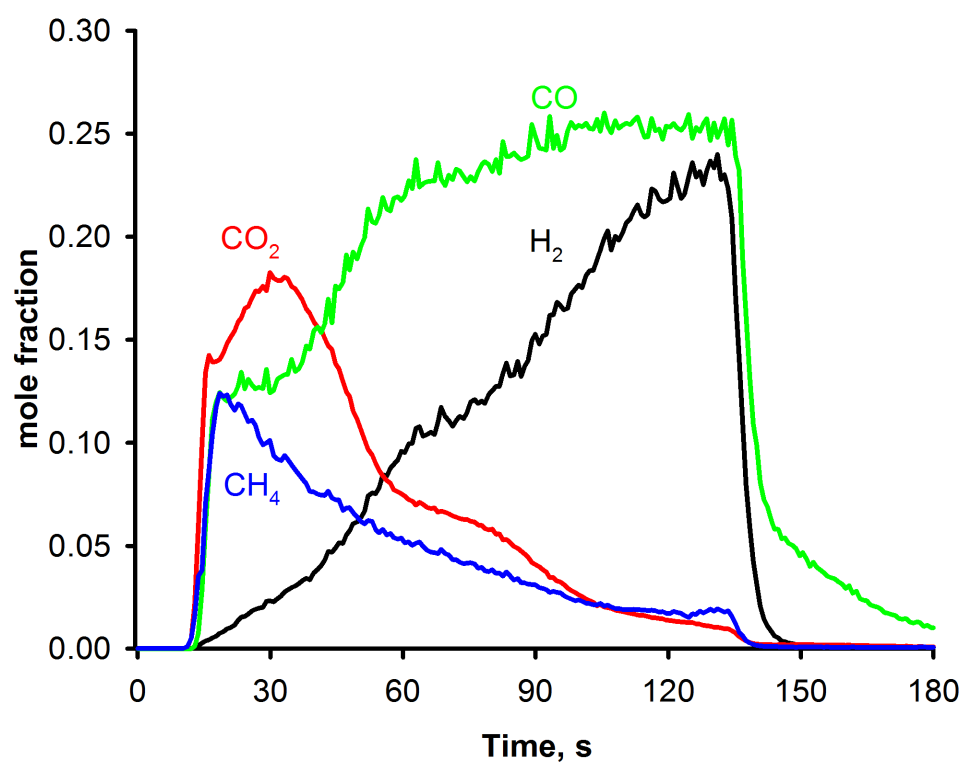


Figure 5.8 Reduction of pyrolusite with 25 % carbon monoxide and 15 % methane at 952 °C.

via a step change in the inlet concentration. The axial dispersion coefficient was calculated by curve fitting of the tracer experiment. We tested helium co-fed with CO as a representative hydrodynamic tracer. However, He passes through the whole reactor, feed lines and analytical section at more rapidly (6s earlier at 808 °C), and with 10 times less dispersion than CO. Instead, and by ensuring that coking was negligible during the reduction with CO, we selected the total carbon fed to the reactor (sum of CO and CO₂) as the tracer. The dispersion coefficient averaged $1 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$, versus $1 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ for helium. The numerical value for the dispersion was the only parameter when modeling the response of the system to a step change in the inlet concentration.

$$\frac{\partial C_{i,gas}}{\partial t} = -\frac{\partial(u_z C_{i,gas})}{\partial z} + D_z \frac{\partial^2 C_{i,gas}}{\partial z^2} + \frac{(1 - \epsilon)}{\epsilon} \sum_j r_{i,j} \quad (5.12)$$

To satisfy the Courant-Friedrichs-Lewy condition, which ensures numerical stability, the time was set at 0,003 s (Equation 5.13).

$$\frac{\Delta t}{\Delta z / u_z} \leq 1 \quad (5.13)$$

To ensure that the kinetic data was obtained in kinetic controlled regime, we evaluated the Mears (Equation 5.14) and Weisz-Prater (Equation 5.15) criteria for external and internal mass transfer limitations, respectively. Mass transfer dominates when the reaction is fast, i.e. when its rate surpasses the rate at which the reactant molecules travel from the bulk to the surface of the solid (external mass transfer) or the transport rates of gas phase species from the surface to the reacting sites located in the pores of the solid.

We considered the largest particle diameter (212 μm) at the highest reaction rate (0,12 $\text{mol m}^{-3} \text{ s}^{-1}$). At this condition, according to the Mears criterion (Eq. 5.14) kinetics control because the ratio of the kinetic to mass transfer rate is $1,3 \times 10^{-5}$, which is several orders of magnitude lower than the threshold criterion.

To calculate the Weisz-Prater number, we assumed that the concentration at the surface of the solid was identical to that of the bulk, and assumed that the internal diffusion was essentially dominated by the Knudsen diffusion. The mean free path of the CO molecules at 952 °C is 367 nm, i.e. greater than the pore diameter (around 4 nm obtained with the BJH method). The resulting Weisz-Prater number was $4,0 \times 10^{-3}$, which is much less than threshold value of 0.3. Thus the reaction was controlled by kinetics not external nor internal mass transfer.

$$\frac{r_A \rho_p R_p n}{k_c C_{Ab}} \leq 0.15 \quad (5.14)$$

$$\frac{r_A R_p^2}{D_e C_{As}} \leq 0.3 \quad (5.15)$$

Modeling the kinetics of the reduction by CO with an irreversible CO reaction (Eq. 6.9), along with the reoxidation of the surface from the bulk (Eq. 6.10) accounts for more than 95 % of the variance in the data (Fig. 5.9). However, the value of the kinetic constant for the direct CO oxidation reaction decreased with temperature (negative activation energy), as expected : The oxygen transfer capacity reached an asymptote with increasing temperature. The elementary step describing the reoxidation of the surface sites with oxygen from the lattice has a positive 55 kJ mol⁻¹ activation energy.

Helfferich [217] established the conditions for apparent negative activation energy : A minimum of one reversible elementary step for which the reverse reaction rate increases more rapidly than the forward one (or non-Arrhenius reactions, e.g. involving radicals or decomposition of a solid). Possible equilibrium elementary steps include adsorption and desorption of CO and/or CO₂ molecules. The negative apparent activation energy would then be explained by the decreasing heat of adsorption of CO with increasing temperature. Carbon monoxide reacts to carbon dioxide at the surface of the oxide (conversion of an oxidized site to a reduced one, where CO₂ is adsorbed). However, since the mass spectrometer detects CO₂ as soon as CO is fed to the reactor, we considered the desorption to be instantaneous. Another possibility for reversibility is the reverse reduction reaction (Eq. 5.16). Indeed, the reduced form of this calcined mineral reduces CO₂ to CO (i.e. the reverse reaction).

$$r_{1,eq} = k'_1 P_{yCO} N_s \theta_{O*} - P_{yCO_2} N_s (1 - \theta_{O*}) / K_1 \quad (5.16)$$

5.3.6 Estimation of adsorbed CO species

Surface species are by nature difficult to observe and quantify. We must rely on simplifying assumptions to model reactions such as the evolution of adsorbed CO with time. One way to do so is to rely on macroscale data such as gas profiles measured by mass spectrometry to estimate these quantities. We previously observed that during mixed methane and carbon monoxide reductions, increasing the temperature led to the presence of a tail after switching the gas from reducing to inert conditions (Fig. 5.8). We observed the same phenomenon when CO reduced calcined pyrolusite. We assumed that the tail of the CO curve during washout

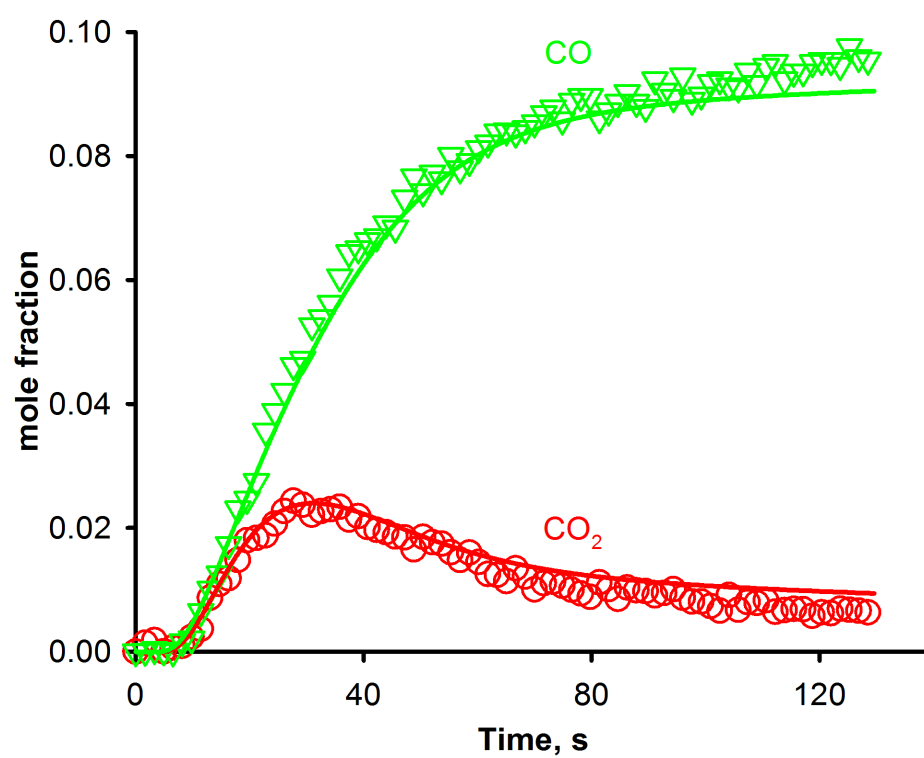


Figure 5.9 The model (solid lines) accounts for 96 % of the variation in the data (red circles and green lower triangles for CO₂ and CO, respectively).

was the result of surface CO species desorbing when switching to inert conditions (Fig. 5.10). At all temperatures, the CO washout curve initially follow exactly that of helium, but starts to diverge when the CO concentration drops, then slowly decreases until it reaches zero. At 814 °C, the difference between the helium and the CO curve is minimal, highlighting the very low surface CO concentration. There is also a general trend for increasing temperatures : The washout curves are similar, but with an increased residual surface CO concentration. However, the CO washout curve at 951 °C, while initially higher, reaches zero faster than that of the lower temperatures. This trend was common to all data obtained at this temperature (2 repeats at each temperature/concentration reduction).

We estimated the adsorbed CO at the end of the reduction by calculating the difference in the area under the washout curves between CO and that of helium at the same temperature. We obtained the number of moles of adsorbed molecules per unit surface area (N_{CO*}) by multiplying the area difference with the total number of moles normalized over the surface area of the bed (BET specific surface times the mass of oxide, i.e. Eq. 5.17). The numerical values ranged from 9 $\mu\text{mol m}^{-2}$ to 61 $\mu\text{mol m}^{-2}$ (Fig 5.11), in agreement with the estimated surface site density of 41 mol m^{-2} . During reduction, the outermost layer of the oxide converts to manganosite (MnO), corresponding to a maximum surface CO concentration of 82 mol m^{-2} , i.e. twice the value for the oxygen surface site density (one unchanged manganese site and one oxygen-depleted site). The calculated CO surface sites densities are consistent with this estimate.

$$N_{CO*} = \frac{PV}{RTS_{BET}m} \int_{t_{switch}}^{t_{wash}} (y_{CO} - y_{He}) dt \quad (5.17)$$

The surface CO density increases with temperature (up to a maximum) and CO partial pressure (Fig 5.11). The total number of adsorbed CO at the end of the reduction increases with temperature from 810 °C to 910 °C, remains almost constant. This result is consistent with theoretical adsorption kinetics, which states that the rate of adsorption is the product of the sticking probability (Eq. 5.18) [218] and the Hertz-Knudsen equation (Eq. 5.19) [219], yielding a function of temperature, partial pressure and surface coverage [220]. The theory further specifies that the effect of temperature is twofold and antagonistic : the rate increases with temperature due to the Arrhenian nature of the sticking probability (S), but the flux of incident molecules (F) decreases with the inverse of the square root of the temperature. However, for a given activation energy, the effect of the Arrhenian term is exponential and is much greater than that due to the sticking probability.

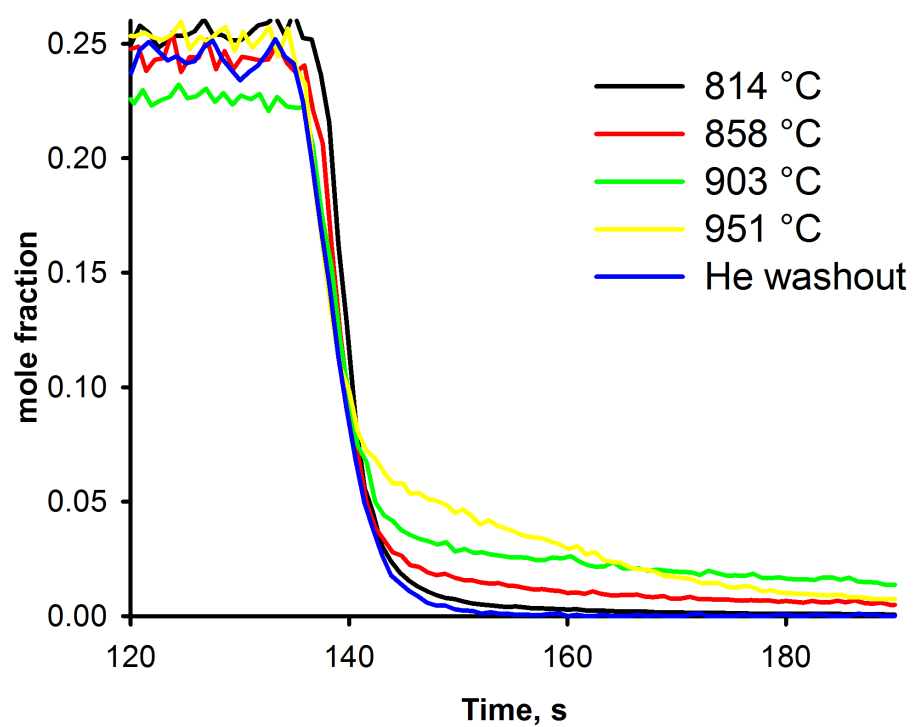


Figure 5.10 The helium washout curve established the baseline from which we calculate the amount of adsorbed CO species desorbing as soon as CO is no longer being fed to the reactor.

$$S = f(\theta) \exp\left(\frac{-E_a}{RT}\right) \quad (5.18)$$

$$F = \frac{P}{(2\pi m_{molec} k_B T)^{1/2}} \quad (5.19)$$

The adsorbed CO coverage at the end of the reduction peaks at approximately 70 % at 910 °C of the available surface, despite the increasing temperature. This could be an indication that the system reached a dynamic adsorption-desorption equilibrium at high surface coverage.

The decreasing surface species concentration for temperature greater than 910 °C was visible on the washout curves (Fig. 5.10) : While being initially higher than the washout curves at lower temperature, the CO dropped more rapidly at 951 °C. This drop in CO at 951 °C can be assigned to multilayered gas molecule adsorption. The upper layers are less bound and desorb more rapidly.

The general conclusion that can be withdrawn from the washout curve analysis is that at the end of the reduction by CO, the surface is probably fully covered with adsorbed CO. In addition, by considering the highest value at 910 °C and 20 vol. % CO as an outlier, we observe a general saturation trend at all conditions indicating that a CO adsorption-desorption equilibrium has been established. The total amount of adsorbed CO almost linearly increases with temperature, and reaches a constant value for temperatures higher or equal to 910 °C. The adsorbed CO peaked at $7 \mu\text{mol m}^{-2}$ when reduced with 15 vol. % CO, $20 \mu\text{mol m}^{-2}$ at 20 vol. % and $55 \mu\text{mol m}^{-2}$ at 25 vol. %.

5.3.7 In situ estimation of the surface site density

We estimated the surface site density by calculating the area under the curve of the initial response (initial CO₂ peak) of the transient reduction of pyrolusite with CO. This estimation relies on two assumptions : i) the surface reaction (Eq. 5.6) is faster than the reaction of oxygen replenishment from the bulk (Eq. 5.4) which is rate limiting; and ii) the solid is not reduced via a shrinking core scheme where the gaseous reactants and products diffuse into a reacted outermost porous solid matrix. Solid-state diffusion governs the reduction of some metal oxides, e.g. wustite reduced by hydrogen [221, 222, 223] and ilmenite reduced by carbon monoxide [141]. In addition, the surface reaction rate constant is 2 orders of magnitudes greater than surface-to-bulk solid-state diffusivities during oxygen uptake of perovskites [224]. The reduction of wustite by hydrogen leads to a nonporous outer shell, where even hydrogen cannot permeate. This phenomenon excludes the shrinking core as the possible reaction

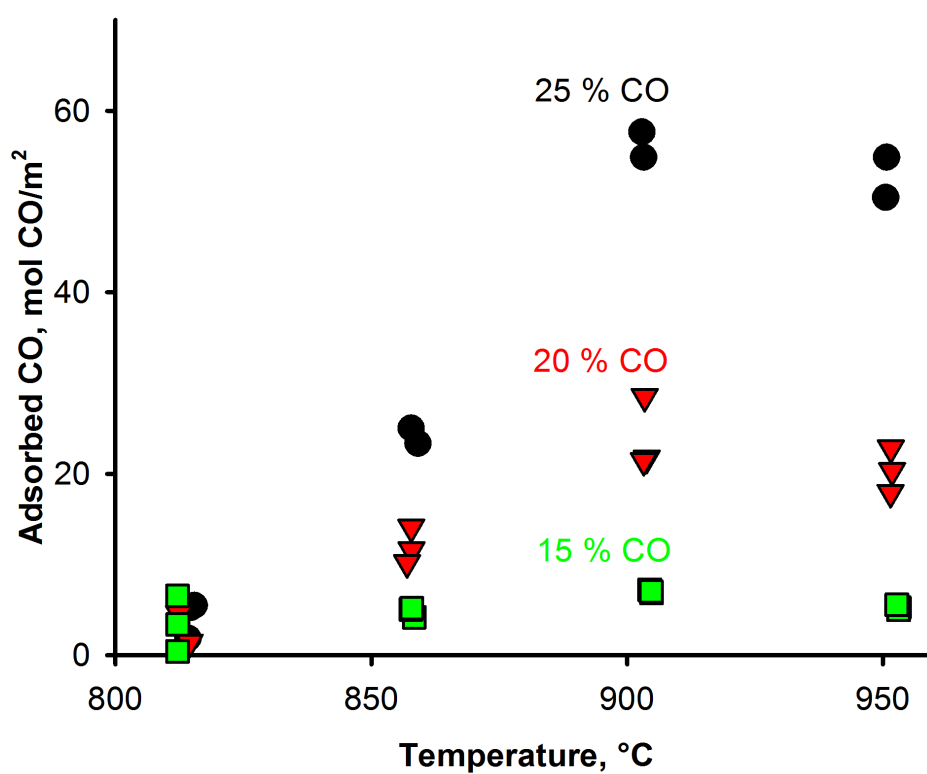


Figure 5.11 Maximum adsorbed CO desorbing during the CO washout at the end of the reduction cycle.

mechanism. However, where solid-state reactions are rate limiting, the diffusion species is an iron cation from the outer surface towards the center of the lattice [221, 222, 223].

To test these assumptions, we used the kinetic model for the reduction of ilmenite with CO [141]. We characterized the reduction of ilmenite with carbon monoxide, with a 2 steps mechanism : i) reaction of CO with surface oxygen and, ii) replenishment of the surface reduced sites by oxygen from the bulk. We assessed the response of ilmenite with a step change in CO due to the surface reaction only, by extinguishing the reaction as soon as the surface oxidized sites were depleted (Fig. 5.12). In this case, the reaction is very fast and limited by external mass transfer, which explains the tailing of the CO₂ concentration. Eliminating this resistance lead to a pure step change with the dispersion. The main result from this modeling experiment is that the surface reaction for the whole bed corresponds to the increasing CO₂ concentration, up to where it reaches its maximum value. This peak can thus be associated with the total available surface in the reactor bed. We can calculate the total number of moles of transferred oxygen during this initial peak to estimate the surface site density (Eq. 5.20). For the reduction of ilmenite, the ratio of the surface and reoxidation reaction rates is greater than 100 for the duration of the reduction.

$$N_s = \frac{PV}{RTS_{BET}m_{cat}} \int y_{CO_2,peak} dt \quad (5.20)$$

Further refining the analysis by neglecting external mass transfer limitations, we confirmed that the surface concentration of oxygen atoms can be estimated by considering the initial peak of the product formed in this simple equimolar reaction. For example, when reducing calcined pyrolusite with carbon monoxide, the CO₂ reaches its maximum value after 21 s, then gradually decreases. Knowing that the surface reaction is fast, and that the global rate of reaction slows when diffusion is predominant, we can assume that this shift between surface and diffusion regimes corresponds to t_{max} . Then, we can artificially extinguish the surface reaction from that point and plot the response of the system by using the axial dispersion coefficient calculated from the hydrodynamic response (Fig. 5.13). This method is equivalent to a simulated CO titration.

The height of the initial peak is a function of the reductant concentration : The higher the CO fed to the reactor, the higher the CO₂ produced. We compared the CO₂ gas profiles with increasing CO concentration. We reduced calcined pyrolusite with carbon monoxide for 2 min at concentrations of 5, 10, 20 and 25 vol. %. The initial CO₂ profile reached a maximum value, highlighting the surface reaction saturation (Fig. 5.14). Reducing calcined pyrolusite with a concentration of 20 vol. % or higher invariably yielded a maximum 3,1 %

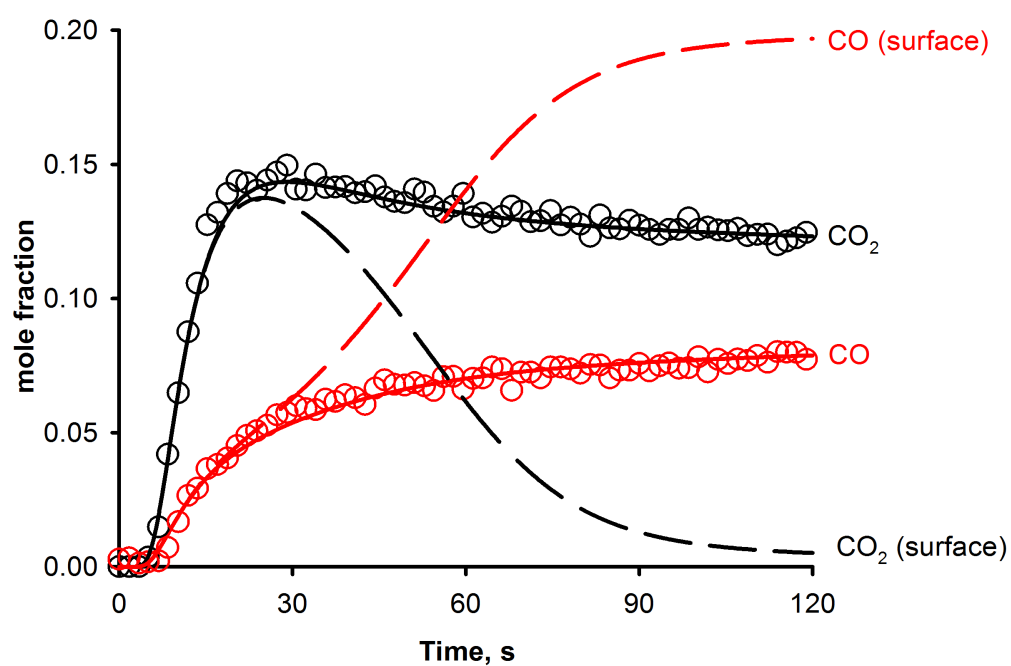


Figure 5.12 The solid lines represent the model with the contribution of the oxygen from the bulk of the lattice. The dashed lines represent the model that considers the surface reaction only. The tailing of the modeled gas profiles is due to the external mass transfer resistance for such fast reactions.

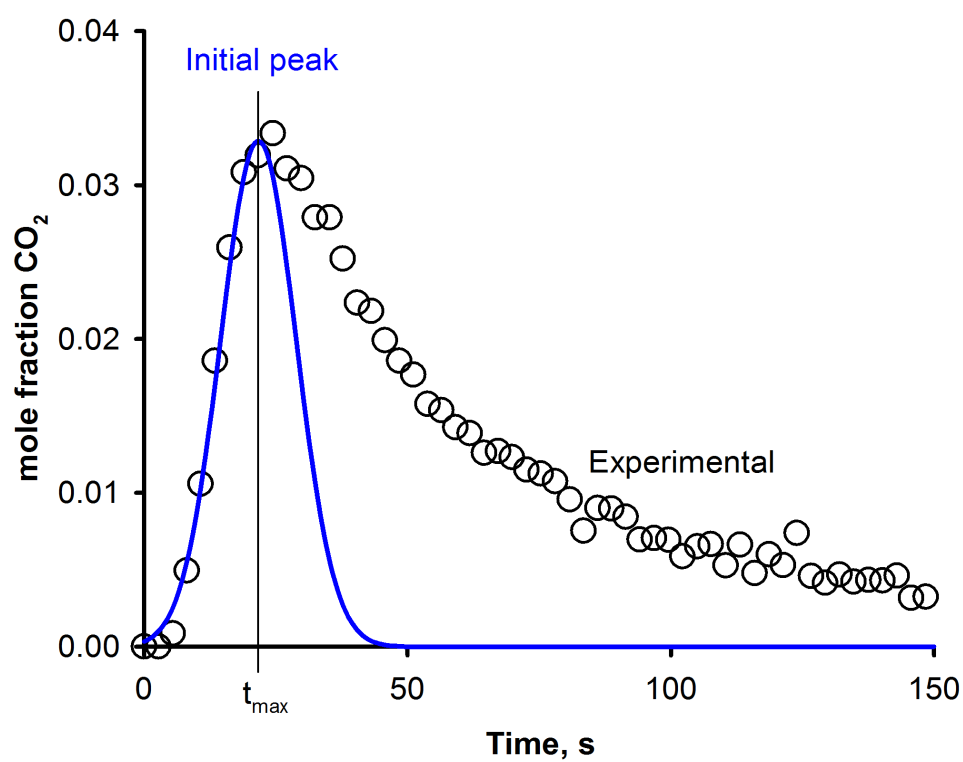


Figure 5.13 We estimate the surface site density from the area under the curve of the initial CO_2 peak.

CO₂ mole fraction. Considering the area under the curve of those simulated titration peak, we calculated the average surface site density (2 repeats for each reduction). The calculated values increased from 27 $\mu\text{mol m}^{-2}$ to 35 $\mu\text{mol m}^{-2}$ for a CO concentration of 5-10 vol. %, followed by an asymptotic 40 $\mu\text{mol m}^{-2}$ value for a CO concentration greater or equal to 20 vol. %. We used this value to characterize the kinetics of the reduction by CO.

This value agrees well with that of Tamura et al. [25], Malloy and Donne [210], but is one order of magnitude greater than that reported by Briand et al. [27]. However, the surface site density is always measured at conditions as close as possible to the planned use of the oxides. In addition, in the case of a chemical measurement, the probe should be the reactant, or very a very similar compounds. Tamura et al. [25] measured the surface site density by monitoring the methane formed at room temperature when reacting hydrated oxides with a Grignard reagent, in the context of their usage in ion-exchange reactions in water. Briand et al. [27] and Wachs and Routray [26] chemisorbed methanol over bulk oxides and monitored the IR spectra and mass variations in a thermogravimetric analyzer at 100 °C. Indeed, the proposed usage for the oxides was the selective oxidation of methanol at 300 °C. Malloy and Donne [210] measured the evolution of surface oxide and hydroxyl sites during the reduction of γ -MnO₂ by chemical titration for a fuel cell application. They partially reduced the manganese oxide with 2-propanol at room temperature and measured the pH variations. The numerical values obtained by those researchers coincide, except in the case of Wachs and Routray [26], an order of magnitude lower. Malloy and Donne [210] measured surface site densities of 11 $\mu\text{mol m}^{-2}$ to 10 $\mu\text{mol m}^{-2}$ for MnO_{1.97} and Mn₂O₃, respectively. Tamura et al. [25] measured surface site densities of 15 $\mu\text{mol m}^{-2}$ to 23 $\mu\text{mol m}^{-2}$ for bulk synthetic MnO₂, while Wachs and Routray [26] obtained a 1,6 $\mu\text{mol m}^{-2}$ value for MnO.

5.4 Conclusion

The recent plunge of the CO₂ trading price constraints further the cost of CLC technology, and as a consequence the cost and performance of the oxygen carrier : mechanical stability, oxygen transfer capacity and reaction kinetics. Pyrolusite is an alternative to ilmenite, because of its superior oxygen transfer capacity, and excellent attrition resistance. We characterized the kinetics of the reduction of calcined pyrolusite with carbon monoxide. The model consists of a surface reaction between CO and an oxidized site, and the replenishment of the reduced sites by oxygen from the lattice. The model accounts for 95 % of the variance in the data. We estimated the surface site density based on the initial CO₂ peak during the reduction by CO (the transient response of the metal oxide undergoing reduction at gradually increasing reductant concentration). The CO₂ peak reached 3 % mole fraction with increa-

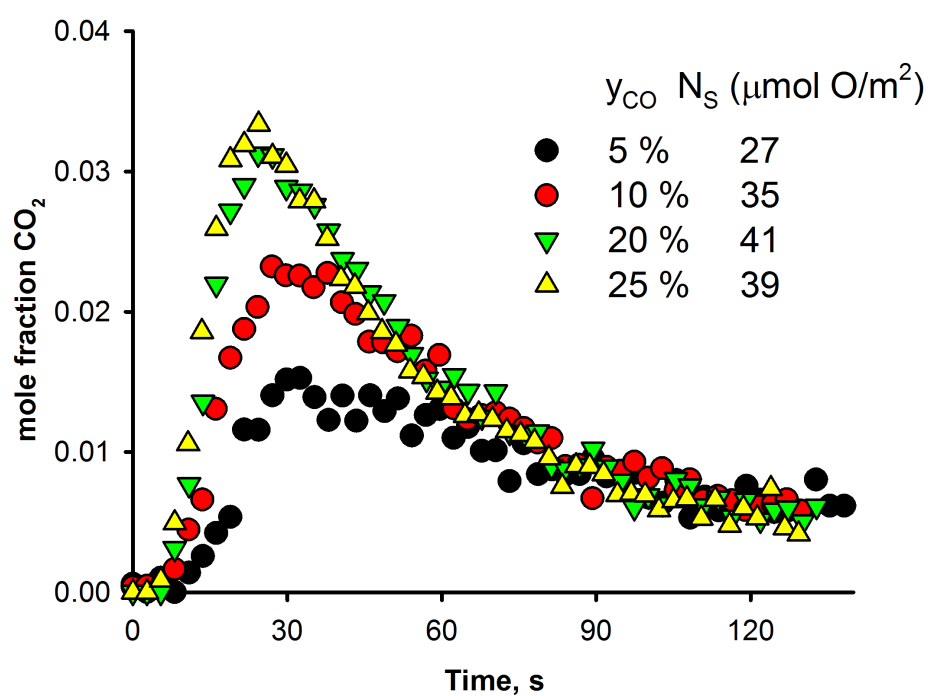


Figure 5.14 Carbon dioxide production when reducing pyrolusite with 5, 10, 20 and 25 % carbon monoxide at 810°C.

sing CO concentrations, which relates to the saturation of the surface reaction with oxygen. We simulated the suppression of the surface reaction using the kinetic and hydrodynamic models. We estimated the surface site density as $41 \mu\text{mol m}^{-2}$ by calculating the area under the CO_2 initial peak, normalized over the total surface of the bed. Simulated *in situ* CO titration has never been reported and usually relies on chemical titration. This method allows to estimate the surface site density without having to rely on a separate experimental setup and using online gas measurements. In addition, the surface site density is obtained at the reaction conditions, and using the reactant as the probe molecule, two necessary conditions for reliable measurements. Our estimation is consistent with measured values from Tamura et al. [25], Briand et al. [27], Wachs and Routray [26]. Similarly, we estimated the adsorbed CO at the end of the 2 min reduction cycle by comparing the washout curves between helium and carbon monoxide when switching between reducing and inert conditions. The adsorbed CO peaked at $55 \mu\text{mol m}^{-2}$ when reduced with 25 vol. % CO for temperature greater than 910°C , corresponding to a 70 % covered surface.

CHAPITRE 6 ARTICLE 3 : CHEMICAL LOOPING SYNGAS FROM CO₂ AND H₂O OVER MANGANESE OXIDE MINERALS

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Article publié dans la revue *Canadian Journal of Chemical Engineering* [69]

Abstract

Rather than sequestering carbon dioxide from the exhaust of chemical looping combustion reactors, together with the water, it could be used as a source of syngas. For the first time, we split water to hydrogen and carbon dioxide to carbon monoxide with a manganese ore. Specific CO production is 10–100 times higher than Sr, Ce, and Fe doped perovskites and Y_{0.5}Sr_{0.5}MnO₃ perovskites. At a contact time of 0,01 s and at temperatures ranging from 810–960 °C the maximum specific CO production was 5,5 mol kg⁻¹. A combined kinetic-axial dispersion hydrodynamic model accounts for 97 % of the variance in the data assuming the reaction rate is first order in CO₂ and surface reduced sites and in equilibrium with the reverse reaction—a first-order reaction in CO with surface oxidized sites. A second reaction accounts for the diffusion of surface oxygen to the bulk lattice. Hydrogen productivity peaked at 4,8 mol kg⁻¹ at 947 °C, which is twice as high as reported in previous studies on CoFe₂O₄ and Al₂O₃ in the hercynite cycle.

6.1 Introduction

Syngas is the first step in gas-to-liquids (GtL) technologies to produce Fischer-Tropsch fuels and methanol. CO and H₂ can be derived from methane, coal, lignocellulosics, and other waste [225]. Steam methane reforming remains the most important source of hydrogen. Alternative technologies to syngas include chemical looping [226, 138], membranes [227, 228, 229, 230], microreactors [231], and plasma [232, 233, 234, 235]. Bi-reforming of methane, a combination of steam and CO₂ reforming, yielding H₂ and CO in a 2 : 1 ratio (i.e. ideal for the production of methanol [236]), is another emerging technology. However, both dry and bi-reforming rely on the use of methane. Chemical looping processes operate above 800 °C and produce a concentrated stream of carbon dioxide and water.

Rather than condensing water and sequestering the CO₂, it could be used as a source of syngas. Reforming combustion gases is an innovative mitigation strategy to add value to a

waste stream. This approach would also overcome the need to use costly noble metal-based catalysts due to their resistance to coking during dry reforming [237].

6.1.1 Water Splitting

Water is a source of hydrogen that is extracted with light, electricity, and high temperatures. A direct current electrolyzes water to hydrogen and oxygen. This endothermic process requires energy, rendering it uneconomic. Solid oxide electrolysis can also electrolyze carbon dioxide into CO and O₂.

Photocatalytic water splitting requires a photo-anode, where the photoelectrons are promoted from the valance to the conduction band, which electrolyzes water [238]. The main challenge for this technology is the use of the entire visible light spectrum as a photon source (i.e. finding and/or modifying photocatalysts of adequate band gap), and separating H₂ and O₂, which are generated in close proximity [238].

Thermochemical and solar-thermal water splitting and carbon dioxide reduction cycles differ only in the way the solid oxide is reduced. Methane, for example, reduces the metal oxide in one reactor, and in a separate vessel, water or carbon dioxide reoxidizes the metal and forms hydrogen and carbon monoxide. Alternatively, in one vessel, the gases can be cycled in the following manner : reduction gases followed by an inert, followed by a oxidizing gas. Solar cycles rely on high temperatures (up to 2000 °C) to reduce the solid. Muhich et al. [239] split water isothermally (harnicyle cycles), with an increase thermodynamic efficiency versus the temperature cycling solar process (ceria redox) with 6 times more H₂ production on a total mass basis.

Hydrogen production ranges between 0.1–1,8 mol kg⁻¹. Le Gal et al. [240] measured 0,144 mole/kg H₂ over CeO₂ at an oxidation temperature of 1000 °C. Yang et al. [241] identified the optimal composition of Sr-doped perovskites prepared by solid-state reaction, which led to a 0,4 mol kg⁻¹ peak H₂ production at 800 °C, with a reduction temperature of 1400 °C [241]. Kodama et al. [242] achieved 1,8 mol kg⁻¹ H₂ in solar thermal cycles with ZrO₂-supported NiFe₂O₄ [243] and reducing the oxide at 1400 °C. Charvin et al. [244] produced up to 4,3 mol kg⁻¹ of H₂ at 575 °C with 30–50 µm FeO particles in solar thermal cycles, with a Fe₃O₄ reduction temperature above 1600 °C.

The thermochemical water splitting processes are more efficient, but they require a reductant (methane, syngas, or a solid fuel). In chemical looping, a solid oxygen carrier is sequentially oxidized and reduced in two interconnected fluidized bed reactors (air and fuel reactors, respectively), avoiding direct contact between the fuel and air, and so generating a concentrated

stream of CO₂ and water (chemical looping combustion, CLC). The CLC processes can be regarded as an oxy-fuel process without the energy penalty associated with air separation. Kang et al. [245] proposed a three-reactor chemical looping process, where the solid oxide is first reduced in the fuel reactor, partially oxidized in a water splitter, and then fully oxidized in the air reactor. This process was further refined by replacing the air reactor with a water splitter (chemical looping water splitting (CLWS) [64].

Many synthetic metal and mixed oxides, bulk and supported, produce hydrogen in thermochemical and solar thermal water splitting cycles. We report for the first time splitting water with manganese ores. To our knowledge, water splitting over oxides of mineral origin has never been reported. Volatile oxides are used in solid-vapour thermochemical CO₂ reduction and water splitting cycles, among them Zn/ZnO at 350 °C [246], as well as SnO₂/SnO [247] Fe-, Cu-, and mixed Cu-Fe can split water, with a maximum of 0,2 mol kg⁻¹ hydrogen production [64]. The U.S. Department of Energy identified copper chloride, ferrite, zinc, and manganese oxide as candidates for solar thermochemical hydrogen production at a target cost of 6 \$/kg [248].

6.1.2 Carbon Dioxide Reduction

CO₂ is an emerging feedstock for : i) fuels (methane, methanol) ; ii) commodity chemicals via hydrogenation (e.g. formaldehyde, formic acid) ; iii) olefins from dehydrogenation of alkanes [236] ; iv) styrene via dehydrogenation of ethylbenzene ; v) dry reforming of methane, alcohols, and glycerol ; and vi) direct splitting into CO. CO₂ inhibits coking of catalysts, increases olefins yield (alkane dehydrogenation), and improves styrene selectivity [236].

Three major axis to split CO₂ are under development : i) thermochemical non-catalytic and catalytic gas-solid CO₂ reduction ; ii) light-driven photocatalytic reduction ; and iii) electrochemical reduction for fuel cells[249]. Similarly to photocatalytic water splitting, CO₂ photocatalysts are unable to split CO₂ under visible light [250]. The main challenge is to split carbon dioxide with the entire visible light spectrum.

Sr, Ce, and Fe-doped perovskites supported on ZrO₂, Al₂O₃, and SiO₂ can split CO₂ (0,068 mol kg⁻¹ [251]). The CeO₂ system has been thoroughly investigated, with CO production reaching 0,079 mmol kg⁻¹ h⁻¹ at 1500 °C [252, 253]. Sr-doped lanthanum manganite perovskites generate up to 0,27 mol kg⁻¹ CO [243].

Dey et al. [254] measured up to 0,76 mol kg⁻¹ CO during CO₂ reduction over Y_{0.5}Sr_{0.5}MnO₃ perovskites at a 900 °C oxidation temperature (and 1400 °C reduction/thermal decomposition temperature), i.e. more than what they had previously obtained with La_{0.5}Ca_{0.5}MnO₃

perovskites ($0,53 \text{ mol kg}^{-1}$ at 1100°C [255]), and more than seven times that measured by Le Gal et al. [240] with CeO_2 at 1000°C .

Catalysts must be at minimum thermally stable and inexpensive to compete with natural gas reforming [256]. Wang et al. [250] reviewed metal-organic frameworks (MOFs) for CO_2 reduction into both CO and small organic molecules. MOFs are inorganic-organic porous structures consisting of linking organic ligands and metal cluster nodes. Adding NH_2 functionality enhances optical absorption and CO_2 adsorption rates [250]. The MOFs, however, are less thermally and hydrolytically stable and cost more. Large-scale and cheap energy production should rely on cheap or free materials, namely dirt (unrefined minerals) [257]. Surprisingly, minerals, with a zero synthesis cost, have been neglected thus far.

6.1.3 Solid Oxides Oxidation-Reduction Rates

Morphological models (“f(X)” laws) characterize the oxidation-reduction kinetics. CaSO_4 reduction in a TGA has been modelled alternatively using Avrami-Erofeyev (A2) [148] and power law (F1) [149] models (Table 6.1). The kinetics of Fe_2O_3 and supported Fe_2O_3 reduction can be characterized using diffusion (D3) [150] and shrinking-core models (R3), [92, 151] respectively. Ilmenite, an iron titanium oxide, has been characterized using a sequence of diffusion (D3), up to a certain degree of reduction, then the R3 model [17]. R3 [92, 154] as well as F0/R1 [153, 151] were used to model the reduction of copper oxide and supported (Al_2O_3) copper oxides. Nickel oxide supported on a NiAl_2O_4 spinel, on bentonite, on yttria-stabilized zirconia (YSZ), as well as on alumina has been characterized using diffusion (D3) [129], shrinking core (R3) [92, 155], and power law models (F1) [92, 156].

Mechanistic models are less common in the CLC literature, and generally rely on semi-empirical laws (e.g. power laws [152, 157]). Brown et al. [89] and Iliuta et al. [155] derived both mechanistic and morphological models to characterize methane oxidation over NiO [155, 89], as well as Perreault and Patience [141] for CO oxidation over ilmenite. Here we derive the kinetics for CO_2 reduction to CO over a reduced manganese oxide mineral.

6.2 Experimental

Pyrolusite (80 % MnO_2) from Central Africa was crushed and sieved to recover 90–106 μm diameter powder. X-ray fluorescence (Bruker/S-4 Pioneer) measured the elemental composition of pyrolusite (Table 6.2). The Scott density of the pyrolusite was $1,78 \text{ g cm}^{-3}$, and an Accupyc 1340 (Micromeritics) gas pycnometer measured the particle density as $4,28 \text{ g cm}^{-3}$. The fresh pyrolusite was amorphous (XRD measurements) with a $7,3 \text{ m}^2 \text{ g}^{-1}$ specific surface

Tableau 6.1 Mathematical expressions of conventional kinetic models based on solid conversion

Models	Differential form $f(X) = 1/k \times dX/dt$
Nucleation models	
P2 power law	$2X^{1/2}$
P3 power law	$3X^{2/3}$
P4 power law	$4X^{3/4}$
A2 Avrami-Erofeyev 2D growth of nuclei	$2(1-X)(-\ln(1-X))^{1/2}$
A3 Avrami-Erofeyev 3D growth of nuclei	$3(1-X)(-\ln(1-X))^{2/3}$
A4 Avrami-Erofeyev	$4(1-X)(-\ln(1-X))^{3/4}$
B1 Prout-Tompkins	$X(1-X)$
Shrinking core models	
R2 Contracting area	$2(1-X)^{1/2}$
R3 Contracting volume	$3(1-X)^{2/3}$
Deceleratory curves	
Zero order (F0/R1)	1
First order (F1)	$(1-X)$
Second order (F2)	$(1-X)^2$
Third order (F3)	$(1-X)^3$
Diffusion	
1D Diffusion (D1)	$(2X)^{-1}$
2D Diffusion (D2)	$-\ln(1-X)^{-1}$
3D Diffusion, Jander (D3)	$3(1-X)^{2/3}(2(1-(1-X)^{1/3}))^{-1}$
3D Diffusion, Ginstling-Brounshtein (D4)	$3(2(1-X)^{-1/3} - 1)^{-1}$

area, measured by a Quantachrome Autosorb-1 gas sorption analyzer.

Calcining the pyrolusite at 850 °C for 1 h under a steady flow of 0.21 L/L (21 vol%) O₂ in Ar increased the crystallinity and produced bixbyite (Mn₂O₃), measured by X-ray diffraction (Figure 6.1; Bruker D8/Discover diffractometer). The BET specific surface increased 32 % to 9,7 m² g⁻¹ after the temperature treatment.

Due to its high reactivity toward CO and H₂, a sample of only 0,0576 g was loaded to a 7 mm ID quartz tube containing a porous quartz frit as a distributor installed at mid-length. The bed height was 0,8 mm. An electrical furnace heated the 28 cm long tube containing pyrolusite from ambient to 800 °C at a 20 °C min⁻¹ rate under 0.21 L/L (21 vol%) O₂. A Hiden QIC-20 quadrupole mass spectrometer measured the gas concentration at 2,5 Hz frequency.

The upward gas flow during the preheating/calcination elutriated the fines by pneumatic transport. The narrowing of the particle size distribution was confirmed quantitatively by a Horiba particle size analyser. The particle size distribution was initially bimodal and it became unimodal after conditioning with a Sauter mean diameter of 98 µm.

The manganese oxide was sequentially oxidized and reduced (5 min cycles) under 0.21 L/L (21 vol%) O₂ (balance Ar), and 0.15 L/L (15 vol%) H₂ (balance Ar), respectively, until oxygen transfer (moles of oxygen transferred per unit mass of sample) in both reduction and oxidation modes was constant. The sample was then successively submitted to reductive and oxidative atmospheres (reduction under 3 concentrations of CO, H₂, CH₄, and binary mixtures thereof, at 800, 850, 900, and 950 °C with 2 repeats at each conditions, yielding > 230 oxidation–reduction cycles), and finally tested for CO₂ reduction and water splitting. The fresh oxide (reduced or oxidized) was inactive, and it activates with time-on-stream to split CO₂.

The stabilized manganese oxide was submitted to CO₂ at three concentrations (10, 15, and 0.25 L/L (25 vol%)) for 5 min, followed by reduction under CO at numerically identical concentrations, and at 800, 850, 900 and 950 °C, with two repeats at each condition. The sample was heated to the reaction temperature under CO₂. We also investigated the effect of the extent of oxidation of the mineral oxide by varying the reoxidation time. The design of experiments included extent of oxidation, temperature, and concentration (Table 6.3).

The water splitting experiments were performed with a simplified methodology. Manganese oxide split a stream of 0.04 L/L (4 vol%) water. The 0.04 L/L (4 vol%) water stream was produced by bubbling argon through a 5,5 cm diameter 11 cm high vessel filled with distilled water at 46 °C. Before each water splitting cycle, hydrogen (20, 30, and 0.40 L/L (40 vol%)) reduced the manganese oxide. Massflow controllers maintained the volumetric gas flowrate at

Tableau 6.2 Elemental composition of fresh pyrolusite as measured by X-ray fluorescence.

Element	weight percent
Mn	62.40
O	26.46
Fe	4.06
Al	3.32
Si	1.62
K	0.81
Ba	0.48
Ni	0.17
Co	0.13
Ti	0.10
Ca	0.09
P	0.09
Zn	0.07
Cu	0.06
Mg	0.04
Na	0.03
S	0.03
Cr	0.02
Sr	0.02

Tableau 6.3 We applied the DOE at 810, 860, 910, and 960 °C. We reduced the calcined pyrolusite with carbon monoxide for 5 min every time.

Runs	CO ₂ %	CO %	Δt_{CO_2} min
1 - 3	25	25	5
4 - 6	25	25	0,5
7 - 9	15	15	5
10 - 12	10	10	5

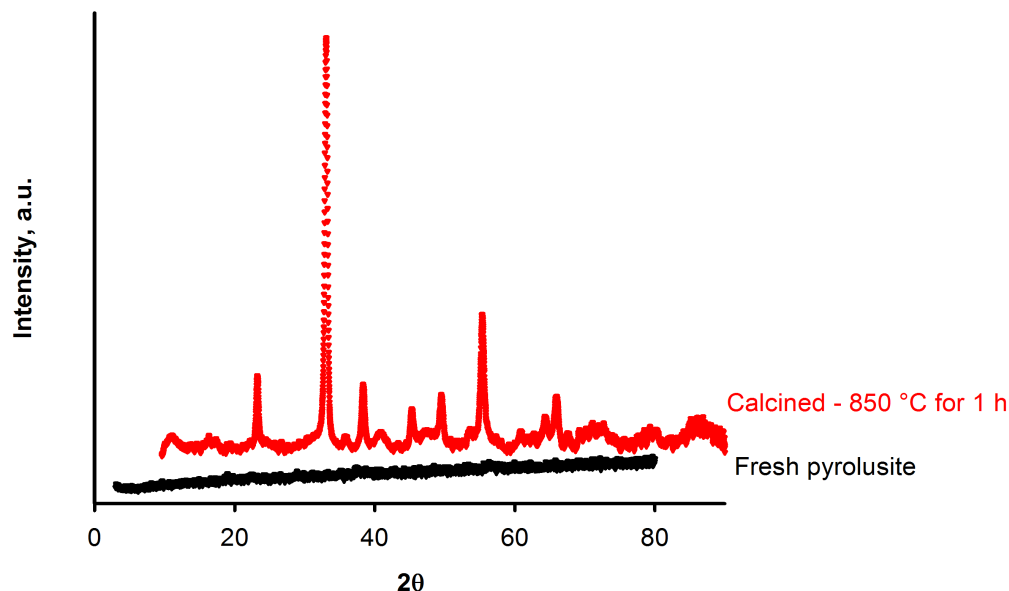


Figure 6.1 The fresh sample is amorphous, and a bixbyite phase results after calcination with air at 850 °C. The diffractogram matches the characteristic peaks of bixbyite (Mn_2O_3).

39,5 mL min⁻¹ (NTP), corresponding to a 1,71 cm s⁻¹ superficial gas velocity.

6.2.1 Hydrodynamic and Kinetic Modelling

We adopted a plug flow model with axial dispersion to characterize the hydrodynamics of the gas phase. The axial dispersion coefficient was estimated based on the response of the exit gas concentration to a concentration step change to the inlet gas composition. First, we compared the gas profiles obtained with various inert tracers (Kr and He) at ambient and reaction conditions (the carbon monoxide bottle contained 0.25 L/L (25 vol%) CO, 0.25 L/L (25 vol%) He, balance Ar), as well as those of the reactants and products at ambient conditions. The inert tracer was discarded since the molecules passed through the reactor and gas analysis section faster than the reactive species, and with less dispersion (lower numerical value for the axial dispersion coefficients). For the CO₂ reduction experiments, we adopted the sum of CO and CO₂ as the tracer. For the water splitting experiments, we relied on the MS krypton signal. The hydrogen bottle contained 0.01 L/L (1 vol%) krypton.

The axial dispersion coefficient was calculated by minimizing the sum of the squared residuals (Marquard-Levenberg algorithm using MATLAB's "lsqcurvefit" function) :

$$\frac{\partial C_{\text{CO}+\text{CO}_2}}{\partial t} = -\frac{\partial(u_z C_{\text{CO}+\text{CO}_2})}{\partial z} + D_z \frac{\partial^2 C_{\text{CO}+\text{CO}_2}}{\partial z^2} \quad (6.1)$$

We measured the temperature profile along the furnace axis and included it in the mole balance to correct the superficial gas velocity.

The Courant condition, to ensure numerical stability, requires the following :

$$\frac{\Delta t}{\Delta z/u_z} \leq 1 \quad (6.2)$$

To achieve higher precision, we created a finer time mesh by a factor of 100, interpolating between successive MS readings. So each time step corresponded to 0,025 Hz.

The mole balance equations for each gas species and the solids phase become the following :

$$\frac{\partial C_{i,gas}}{\partial t} = -\frac{\partial(u_z C_{i,gas})}{\partial z} + D_z \frac{\partial^2 C_{i,gas}}{\partial z^2} + \frac{(1-\epsilon)}{\epsilon} \sum_j r_{i,j} \quad (6.3)$$

$$\frac{\partial C_{i,solid}}{\partial t} = \sum_j r_{i,j} \quad (6.4)$$

A complementary kinetic model was determined following the Johnson-Mehl-Avrami-Erofeev-Kolmogorov equations. The solid conversion was calculated by considering the mole balance on the transferred oxygen and by deconvoluting the gas phase data. Eighteen known models were tested and a choice of the most probable was made on the basis of the norm of the sum of squared residuals.

6.3 Results and discussion

6.3.1 Carbon Dioxide Reduction

In most experiments, a stream of CO in Ar reduced the manganese oxide for 5 min, followed by a 5 min purge of Ar and then 5 min of CO₂ (Figure 6.2). The first three cycles contained 0.25 L/L (25 vol%) CO in the reduction step and 0.25 L/L (25 vol%) CO₂ in the oxidation. The next three cycles contained 0.15 L/L (15 vol%) CO and 0.15 L/L (15 vol%) CO₂ in the reduction and oxidation cycles. Finally, in the last 3 cycles, we reduced the concentration of both CO and CO₂ to 0.10 L/L (10 vol%).

The CO and CO₂ MS signals rise instantaneously, indicating that axial dispersion is small ($1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$). The CO reaches a maximum of almost 10 % about 7 s after the MS initially

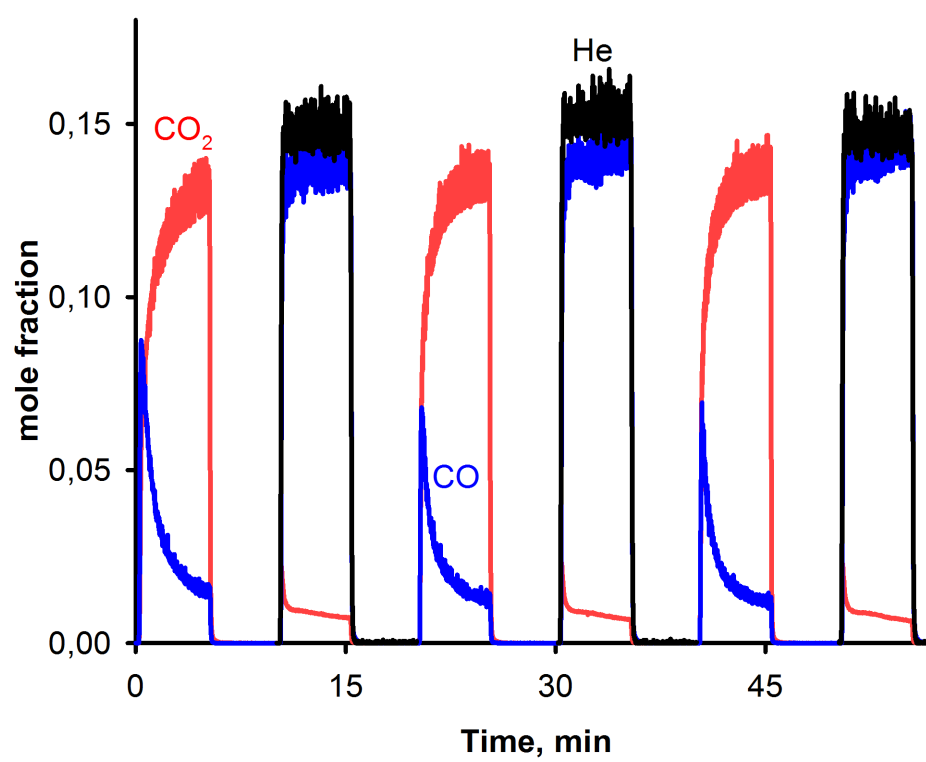


Figure 6.2 15 % CO_2 oxidized the ore (red curve) and 15 % CO reduced it (blue curve).

detects CO (Figure 6.3). After reaching the peak value, the signal drops steadily over the next 5 min to about 2 %. The CO₂ signal rises proportionately with the drop in CO after the peak. The initial large increase in CO indicates that CO₂ reacts to fill the vacant sites. Two mechanisms can account for the drop in CO concentration with time : either surface layers become saturated with oxygen (diffusion limitation), or the reaction is controlled by the equilibrium between the gas and surface oxide species.

The CO productivity is the product of the average CO mole fraction over one cycle and the molar flow rate, divided by the mass of the manganese oxide. The productivity increased almost proportionally with the inlet CO₂ concentration (Figure 6.4). The specific CO production rate at 960 °C was 2,5 mol kg⁻¹ with 0.10 L/L (10 vol%) CO₂ and it was 5,0 mol kg⁻¹ with 0.25 L/L (25 vol%). The productivity increases by 40 % from 810–960 °C.

The upward facing yellow triangles represent the specific CO production . The productivity over Mn₃O₄ reduced under 0.15 L/L (15 vol%) CO and reoxidized under 0.10 L/L (10 vol%) CO₂ is intermediate between the values that we measured at 0.10 L/L (10 vol%) and 0.15 L/L (15 vol%) (CO and CO₂ during the reduction and oxidation cycles), which confirms that the reduction cycle preceding the reoxidation step affects the CO productivity.

For a system composed solely of manganese phases (MnO₂, MnO, Mn₃O₄, and Mn), CO, CO₂, and coke (excluding carbides and carbonyls), thermodynamics predict no more than 0.006 mol/mol (0.6 mol%) CO at 800 °C. Surprisingly, after 20 s the CO mole fraction at the exit reached 0.20 L/L (20 vol%) (Figure 6.5). This high CO concentration resulted after the oxide was submitted to an asymmetric cycling (extended reduction cycle and a short oxidation) in which the sample was reduced by 0.25 L/L (25 vol%) CO for 5 min and reoxidized for only 30 s with 0.25 L/L (25 vol%) CO₂. The instantaneous CO peaks increased with a decreasing extent of oxidation of the manganese oxide (Figure 6.5). When the average extent of oxidation of the oxide was 42 % (i.e. 58 % reduced), the CO reached 0.20 L/L (20 vol%), while it only reached 0.14 L/L (14 vol%) at 49 %. This trend is consistent with our expectations of producing more CO over a more reduced oxide.

The specific production of CO reached a maximum of 5,5 mol kg⁻¹ at 957 °C during the asymmetric cycling tests at 957 °C (Figure 6.4), which is 10–100 times greater than in other studies.[255, 254, 251] This yield was measured when reoxidizing the MnO under 0.15 L/L (15 vol%) CO₂ after having reduced Mn₃O₄ under 0.25 L/L (25 vol%) CO (5 min). This CO production corresponds to transferring 8,8 % of the mass of the MnO as oxygen (from the gas phase to the solid), which is greater than the theoretical mass transfer for the MnO/Mn₃O₄ couple (7 %), but less than that associated with the MnO/Mn₂O₃ couple (10 %). Thermodynamically, CO is unlikely to reduce Mn₃O₄ further than MnO even at 960 °C. Instead, the

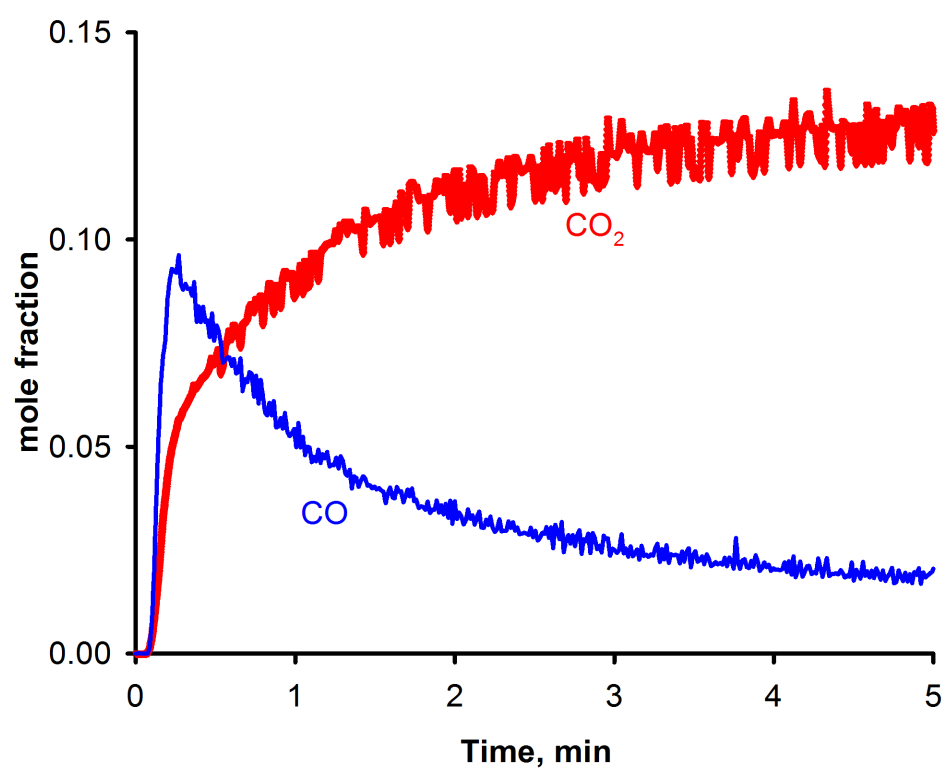


Figure 6.3 Reoxidation of a maximally overreduced sample (40 % reduced) under 15 % CO₂ at 958 °C.

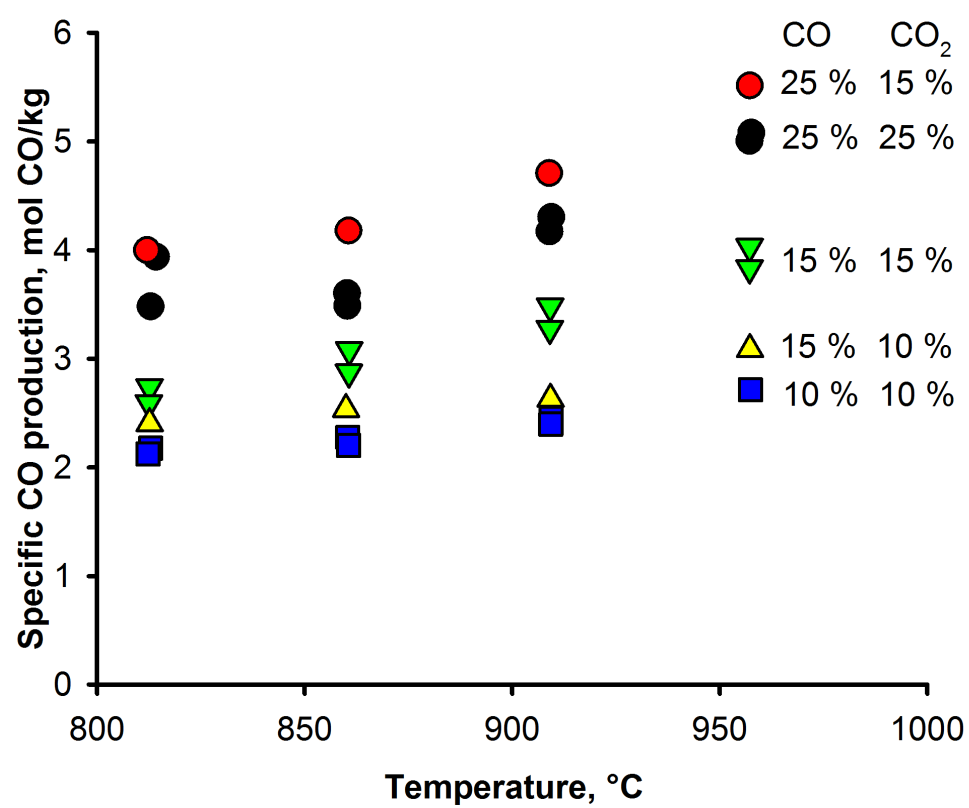


Figure 6.4 CO produced during CO₂ reoxidation cycles between 815–960 °C.

oxide should coke and form manganese carbides or carbonates (MnCO_3).

The CO productivity varies according to the dosing conditions—time, temperature, and concentration of CO and CO_2 (Figure 6.6). During cycles 2 and 3 after the initial ramp to the operating temperature, the specific CO productivity with 0.25 L/L (25 vol%) CO and CO_2 varies from 3,5 mol CO kg^{-1} at a low temperature to 5 mol CO kg^{-1} at a high temperature. The production drops by as much as 5 times during cycles 4–6 with a 30 s oxidation cycle with CO_2 . Temperature had less of an effect at shorter oxidation cycle times and the productivity increased from cycles 4 to 6. The specific CO productivity reached a maximum at cycle 7, for which the oxidation time returned to 5 min with 0.25 L/L (25 vol%) CO during the reduction cycle and only 0.15 L/L (15 vol%) CO_2 in the oxidation cycle. The drop in CO productivity with each following cycle is due to both the changing conditions and the extent to which Mn_xO_y is oxidized.

CO and CO_2 form an equilibrium with Mn_xO_y . We calculated the equilibrium constant by measuring the exit concentrations at the end of the 40 min temperature ramp while we fed 0.25 L/L (25 vol%) CO_2 . The constant varied from 0.042 at 860 °C, 0.056 at 909 °C, and 0.063 at 958 °C.

The fresh oxide (reduced or oxidized) was inactive and it activates with time-on-stream to split CO_2 . While the BET specific surface dropped by 24 % to 1,8 m^2g^{-1} during aging of the oxide, the other textural differences between the fresh and used oxide were negligible : both pore volume and pore radius were constant at 0,04 cm^3g^{-1} and 1,5 nm, respectively. While polishing and cutting the particles for SEM-EDS elemental mapping, the interior became hollow. This weakening of the interior structure may be attributed to the repeated reduction-oxidation cycles. The particle density of the aged oxide increased to 5000 kg m^{-3} .

We assumed that the main effect of the aging process was to render active sites and promoters accessible, due to the migration of these species or by an increase in the number of small channels leading to these sites. Potassium is particularly interesting because alkali metals are known to activate CO_2 : CO_2 chemisorbs over alkali-covered Pd, while it does not on clean Pd surfaces [258, 216]. In addition, alkali-covered surfaces promote the dissociative adsorption of CO_2 (with $\text{CO}_2^{\delta-}$ as an intermediate activated state) into CO and O, with atomic oxygen migrating in the bulk at elevated temperatures [212].

We tested various alternative hypotheses to explain the high CO specific productivity of the aged oxide : i) coking during reduction with CO and CO_2 gasification ; ii) CO production via the formation of potassium carbonate ; and iii) CO production via CO_2 splitting over metallic iron. We rejected the first postulate : Thermodynamics predicts that all of the CO will form CO_2 , manganese carbides, and coke. However, after reducing the oxide with CO

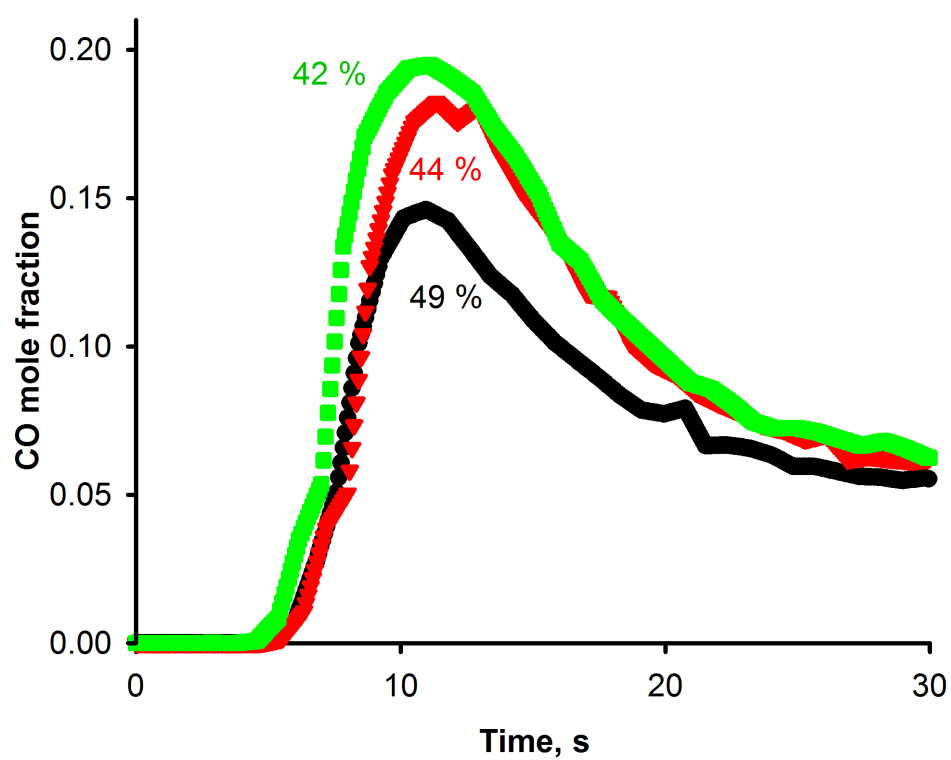


Figure 6.5 CO profiles as a function of the initial extent of oxidation at 812°C for 30 s reoxidation cycles (5 min reduction cycles).

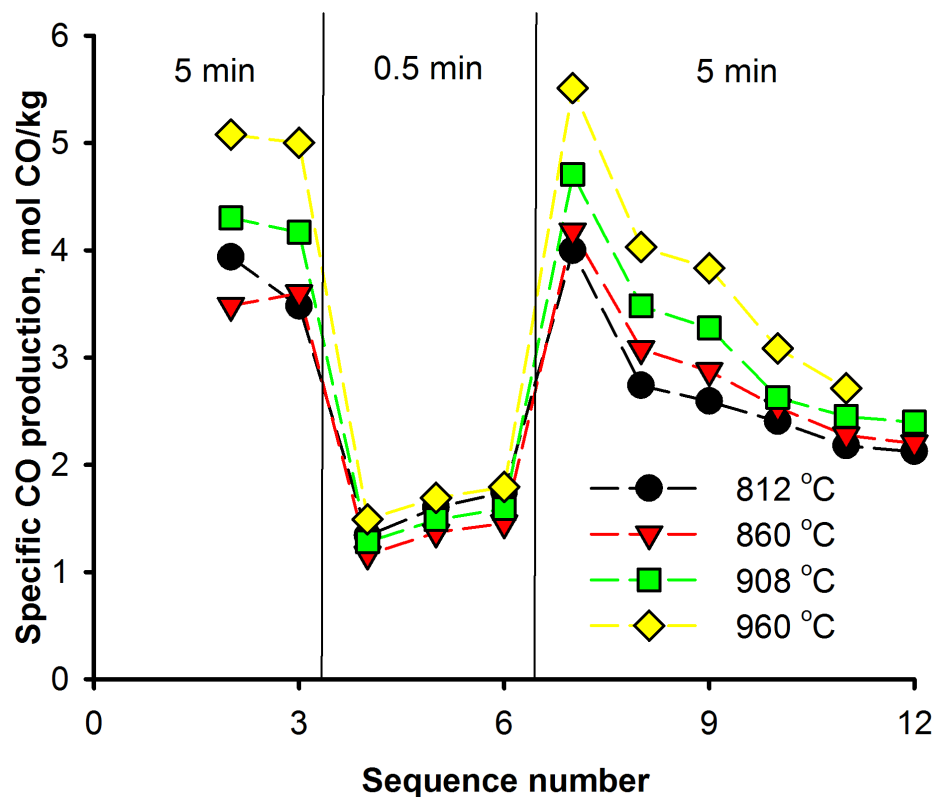


Figure 6.6 Initially, the solid was ramped under CO_2 to reaction temperature and then dosed with 0.25 L/L (25 vol%) CO for 5 min (1). The second two cycles dosed 0.25 L/L (25 vol%) CO and 0.25 L/L (25 vol%) CO_2 sequentially (2,3). In cycles 4–6, a stream of 0.25 L/L (25 vol%) CO_2 oxidized the Mn_xO_y for 30 s followed by 0.25 L/L (25 vol%) CO for 5 min. Dose times for cycles 7–12 were 5 min. The feed concentrations of CO and CO_2 were 0.15 L/L (15 vol%) for cycles 7–9 and 0.10 L/L (10 vol%) for cycles 10–12.

and reoxidizing it with O_2 , coke represented < 0.0001 g/g (0.01 %) of the mass of the oxide, or 0.002 mol/mol (0.2 mol%) of the total CO fed to the reactor. We tested ii) and iii) with a mole balance and equilibrium composition calculations using the elemental composition measured by XRF. Potassium carbonate forms while it is dosed with CO_2 , but the amount of potassium is insufficient to account for the CO. Moreover, it is unlikely to survive the high temperatures because K_2O is unstable and an equilibrium exists between the solid phase and the gaseous $K_{(g)}$ and $O_{2(g)}$ decomposition products. Iron is an active metal but could only account for 18 % of the CO if it were present, and the XRD spectrum shows no iron. After the carbon dioxide reduction cycle, hausmannite (Mn_3O_4) dominates (90 % of the spectrum). We attribute the high reactivity solely to the potassium promoters.

6.3.2 Kinetic Modelling of Carbon Dioxide Reoxidation

We postulate that the kinetics of the carbon dioxide reduction follows an alkali-promoted redox mechanism [212]. We assume that CO_2 is activated into CO_2^- over potassium atoms, then dissociates into CO and atomic surface oxygen (Equations (6.5, 6.6)) :



Assuming that the activated species reacts instantaneously to carbon monoxide and surface oxygen, the net pseudo-first reaction step can be modelled as a surface reaction independent of the promoter.

We postulate that the oxidation reaction rate depends on the CO_2 partial pressure and the extent that the manganese is oxidized, which translates to surface oxygen concentration as well as bulk oxygen concentration (and vacancies). We characterize the kinetics by assuming that the CO_2 reacts on the surface and the newly-formed surface oxygen diffuses into the lattice.



MnO has a rocksalt structure [259] with three surface sites : manganese, reduced sites (oxygen

vacancy), and oxidized sites (Figure 6.7). We assume the surface is nonpolar (100) with no reconstruction or relaxation of the surface atoms.

A CO_2 molecule can reoxidize the surface by first bonding with manganese, or via a vacant site adjacent to the Mn (neglecting possible steric hindrance effects). Whether the carbon bonds with Mn or the oxygen from the CO_2 occupies a vacancy, the reaction rate expression is the same. We apply the mass action law and express the rate law as a function of the product of the initial surface concentration of oxygen vacancies (or Mn sites). This approach is similar to that of Dekker et al. [260]. Whereas Dekker et al. [260] considered a lumped concentration of removable oxygen, we separate the surface reaction and lattice diffusion phenomena as follows :

$$r_1 = \frac{PN_s}{RT} k'_1 (y_{\text{CO}_2} \theta_* - \frac{y_{\text{CO}} \theta_{\text{O}^*}}{K_1}) \quad (6.9)$$

$$r_2 = k'_2 (N_s \theta_{\text{O}^*}) (C_{\text{V}_\text{O}} (1 - \gamma_{\text{O}_b})) \quad (6.10)$$

The quasi-chemical reaction representing the reoxidation of the bulk can be considered a diffusional phenomenon. However, to simplify the treatment of the oxygen diffusion through the lattice, we assigned a lumped oxidation state for the bulk (to avoid treating the solid as the product of successive layers of different extents of oxidation) and a pseudo-kinetic constant to characterize the diffusion through the surface. The driving force for diffusion is the surface oxygen site coverage since the normalized bulk oxygen concentration is almost constant over a short reoxidation period. The concentration of oxygen vacancies appearing in Equation (6.10) was estimated by considering the thermodynamics of Schottky defects (2.4 eV oxygen vacancies energy formation in the bulk [261]), and the stoichiometry of the oxide (here in its reduced form, MnO), its density, and its molecular mass :

$$C_{\text{V}_\text{O}} = \frac{n}{N} \frac{N_{\text{Av}} \rho_{\text{MnO}}}{M_{\text{MnO}}} = \frac{N_{\text{Av}} \rho_{\text{MnO}}}{M_{\text{MnO}}} \exp \frac{-\Delta E_f}{2k_B T} \quad (6.11)$$

The surface site density, N_s in Equation (6.10), represents the concentration of oxygen. To measure this value requires a probe molecule as well as experimental conditions as close as possible to the reaction conditions. Tamura et al. [25] proposed Grignard's reagent to measure the surface hydroxyl sites by monitoring the methane formed at room temperature for metal oxides involved in ion-exchange reactions in water. Briand et al. [27] and Wachs and Routray [26] measured the surface site density of metal oxides that partially oxidize methanol at 300 °C. They chemisorbed methanol and monitored the IR spectra and mass of the sample in a thermogravimetric analyzer at 100 °C. Here, we consider the surface site

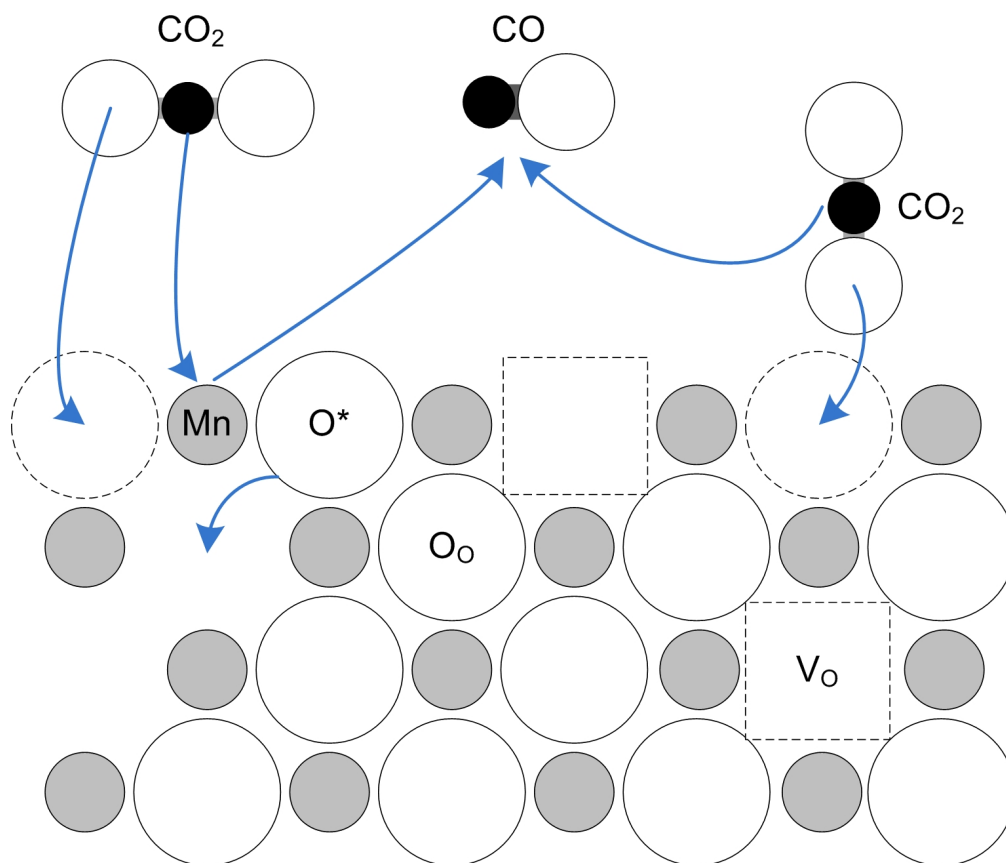


Figure 6.7 Simplified reaction mechanism for the reoxidation of manganosite under carbon dioxide.

density as a fitted parameter. At high temperatures, CO or H₂ reacts with subsurface atoms rendering the titration methods inaccurate. Instead of relying on experimental values for the surface site density, we compare our fitted value with the measurements of Tamura et al. [25] and Wachs and Routray [26] to substantiate the value. The evolution of the surface site density over the oxidation cycle was estimated by taking the product of the initial surface site density (a parameter) and the surface coverage.

The bulk concentration of removable oxygen was selected to represent the theoretical oxygen transfer capacity and the bulk metal oxide density. The surface and bulk oxygen concentrations are as follows :

$$C_{O*} = N_s \theta_{O*} \quad (6.12)$$

$$C_{O_b} = N_r \gamma_{O_b} = \frac{R_{O,th} \rho_b}{M_O} \gamma_{O_b} \quad (6.13)$$

The kinetic model (Equations (6.7, 6.8)) involves four parameters : three kinetic constants and the surface site density. The calculated surface site density (Figure 6.8) increased with temperature, while it was independent of both CO₂ concentration and extent of oxidation. N_s ranged from 0.1–0.8 mmol m⁻² (Figure 6.8), as much as 500 times greater than the value reported by Wachs and Routray[26] by methanol adsorption with bulk MnO, and 35 times greater than that reported by Tamura et al. [25] The large differences between these values are due, in part, to the source of MnO (mineral origin) and the operating temperature. High temperatures open up subsurface layers and increase the mobility/diffusivity of the upper sublayer. Moreover, cycling between oxidation and reduction may modify the surface site density and porosity.

The kinetic model accounts for at least 90 % of the data but R^2 is typically closer to 0.97 (Figures 6.9, 6.10). The reaction rate is extremely fast and the first order rate constant is about 60 s⁻¹ : consider that when we switch the feed gas to CO₂, as much as 50 % of it reacts in the first 10 s. The bed height was 0.8 mm and the superficial gas velocity was 72 mm s⁻¹ (on average). So, the contact time between the feed gas and bed was only 0.012 s. The activation energy for the forward reaction (Equation (6.9)) is essentially zero. The activation energy of the quasi-chemical reoxidation of the bulk is 89 kJ mol⁻¹.

The Gibbs free energy of the oxidation of MnO by CO₂ equals 63 kJ mol⁻¹ at 25 °C. Calculation of the equilibrium constants yielded a line of slope equal to 43 kJ mol⁻¹, which agrees closely with the best fit value we derived from the rate law equation (Equation (6.9)) at

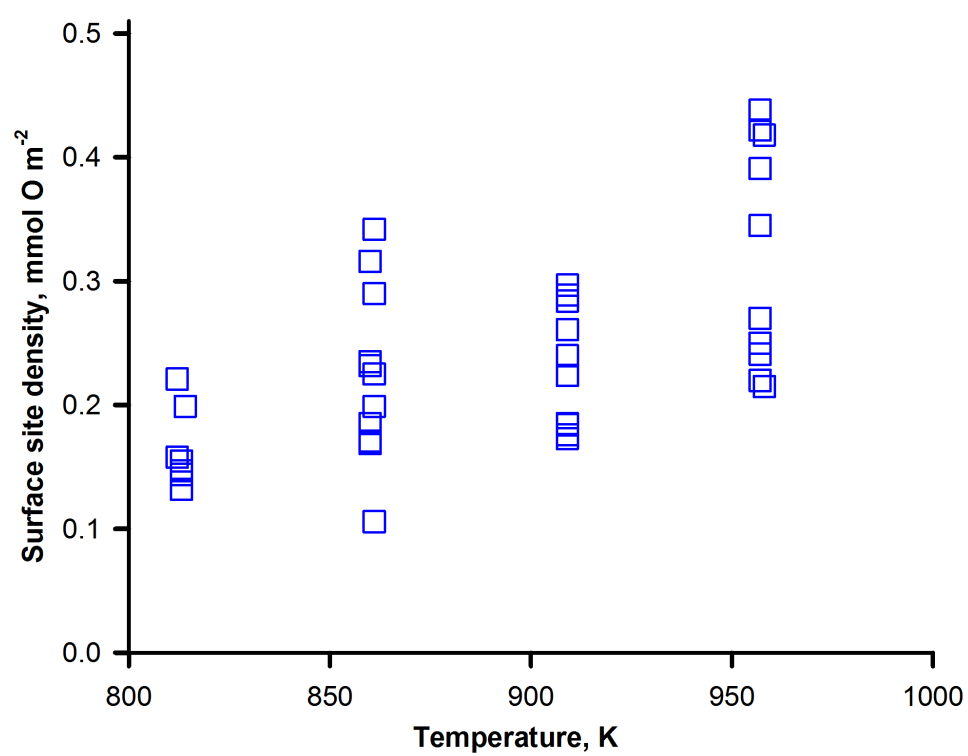


Figure 6.8 Calculated surface site densities as a function of reoxidation temperature.

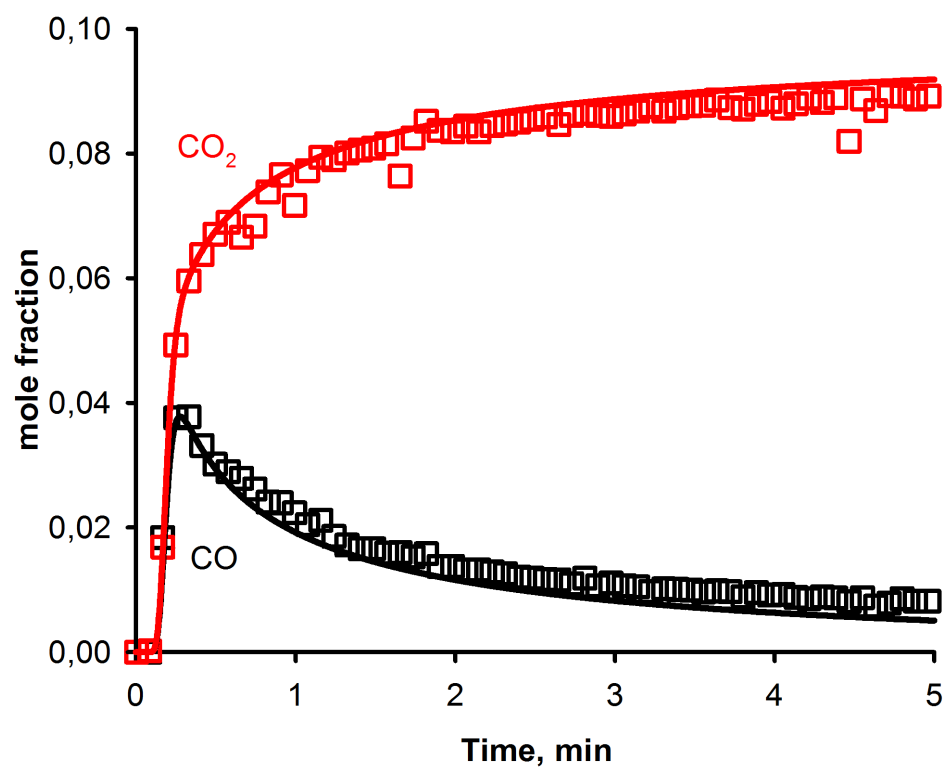


Figure 6.9 The model (solid line) accounts for 90 % of the variance in the experimental data (symbols) recorded by the MS with 10 % CO during the reduction cycle at 860 °C and 97 % of the variance for the oxidation experiments with 10 % CO_2 .

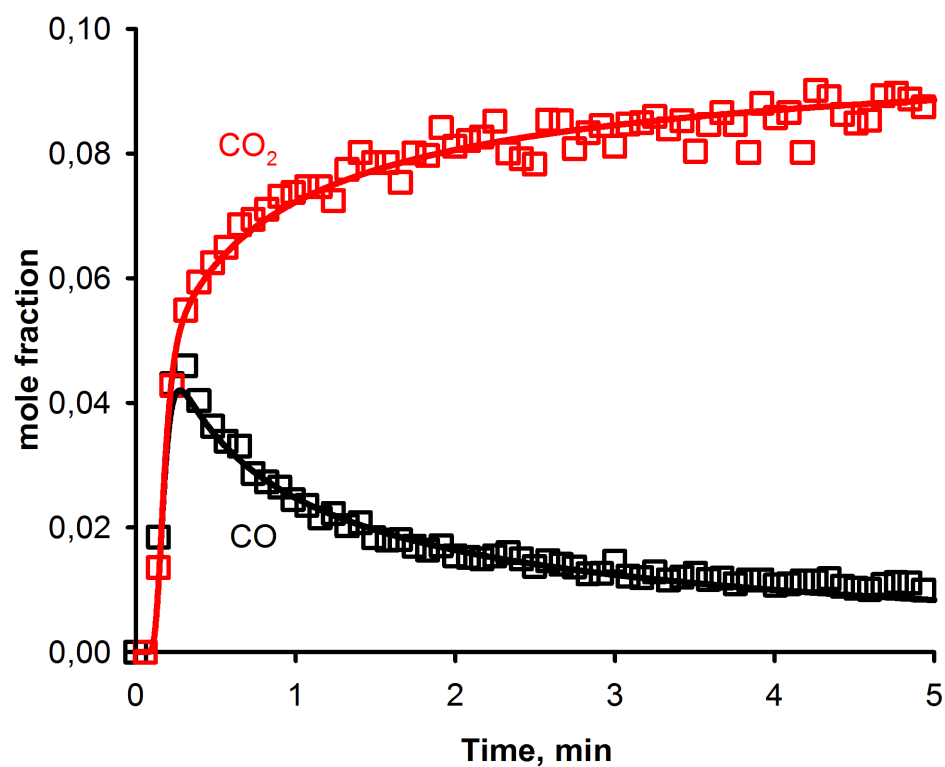


Figure 6.10 The model (solid line) accounts for 97 % of the variance in the experimental data (symbols) recorded by the MS with 10 % CO during the reduction cycle at 960 °C and 97 % of the variance for the oxidation experiments with 10 % CO_2 .

42 kJ mol⁻¹.

Morphological models were also tested to fit the evolution of the conversion of the manganese oxide during CO₂ reoxidation. In this case, the solid conversion was calculated from the deconvoluted gas phase profiles to avoid confusing solid conversions with the hydrodynamics. We tested 17 morphological models, based on the solid conversion calculated from the oxygen mole balance, by plotting the derivative of the solid conversion as a function of the differential form of the $f(X)$ expressions, and selecting those for which the slope is a straight line (and kC^n equals the slope).

Out of the 17 models tested, the third-order power law (F3) fit the solid conversion best. However, the model was unable to characterize the solid conversion for over-reduced pyrolusite, nor for the short 30 s cycles. The F3 model relates the rate of solid conversion to the third power of the remaining unconverted solid, and is restricted to surface phenomena [262]. We included a reaction order with respect to the CO₂ concentration to account for gas phase chemistry as outlined by Moghtaderi and Song [151] :

$$\frac{dX}{dt} = kC^n f(X) \quad (6.14)$$

The kC^n numerical value was first extracted by plotting the derivative of the solid conversion against the $f(X)$ expressions, then the reaction order and apparent kinetic constant were calculated by plotting the logarithm of kC^n against that of the initial concentration (Figure 6.11). The reaction order with respect to the CO₂ was taken as the slope, and the intercepts yielded the kinetic constants at a given temperature. The model accounted for between 62–99 % of the variance in the data.

Excluding the 813 °C data, which are *sui generis*, the activation energy is 48 kJ mol⁻¹, with an average of 1.2 for the reaction order of CO₂. The first CO₂ splitting cycles after the initial temperature ramp from ambient to 800 °C yielded a higher than expected productivity (when compared to the overall trend). This difference can be attributed to the presence of physisorbed CO₂ from the extended temperature ramp under CO₂. In their oxidized forms, manganese oxides can trap CO₂ at its surface without reducing it, releasing it with a further surface modification (e.g. oxidation or reduction). For this reason, we excluded those data points from the kinetic analysis.

6.3.3 Water Splitting

We conducted similar experiments with water and hydrogen as we did for carbon dioxide and carbon monoxide. During the ramp up to reaction temperature, we fed a gas stream

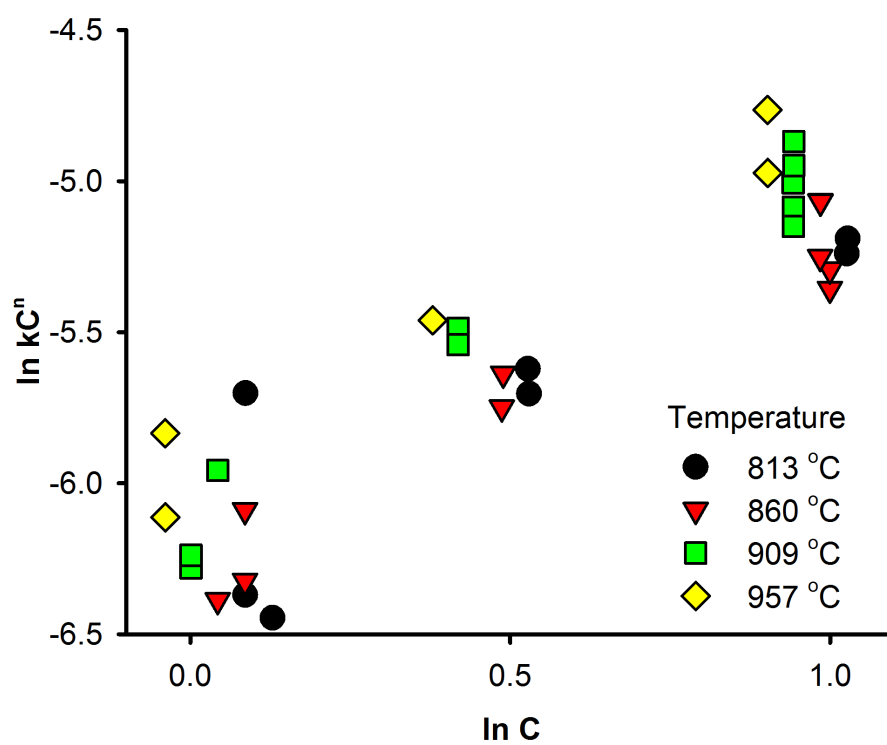


Figure 6.11 Natural logarithm of kC^n as a function of gas concentration.

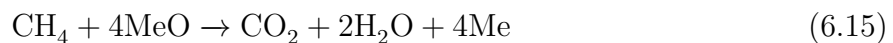
containing 0.04 mol/mol (4 mol%) fraction of water vapour in argon. We switched directly to a stream containing of 18, 29, and 0.39 L/L (39 vol%) hydrogen for 5 min (no intervening purge with argon). A 5 min argon purge followed the hydrogen reduction step (Figure 6.12).

The mass spectrometer detected hydrogen as soon as we switched from the argon purge to the stream containing water vapour. The hydrogen concentration increased much more slowly than for CO and then dropped slowly as the water concentration began to increase. When we switched to hydrogen, the water concentration continued to increase, and in the case of 847 °C, the MS signal for water dropped at the same time for all experiments, at around 7 min.

Hydrogen generation reached a maximum of 4,8 mol kg⁻¹ at 947 °C (Figure 6.13), but it was essentially independent of the hydrogen concentration. It increases almost linearly with temperature. The hydrogen yield reached almost three times that of Kodama et al. [242] and twice as much as reported Muhich et al. [239] at 1000 °C based on the hercynite cycle, which reduces the solid solely with heat (solar cycle).

6.3.4 Chemical Looping Combustion with Carbon Dioxide Reductor and Water Splitter

In chemical looping, fuel (natural gas, biomass, coal) reduces the metal oxide to produce a concentrated stream of CO₂ and H₂O. The exit of the fuel reactor is at high temperature and activated (aged) pyrolusite could split both carbon dioxide and water (Figure 6.14). The advantage of this configuration over other processes is that it produces energy and syngas simultaneously. Other studies have focussed on hydrogen and sacrificed the energy component of the technology when they proposed the chemical looping water splitter (CLWS) [64]. The CLWS is limited thermodynamically : the net energy input, independent of the metal oxide, equals the enthalpy change of the combined steam-methane reforming and water-gas shift reaction. For example, for a generic metal oxide (MeO), the metal oxide reduction reaction under methane (Equation (6.15)), and the water splitting reaction (Equation (6.16)) are as follows :



Adding Equations (6.15, 6.16) leads to the combined steam-methane reforming and water-gas

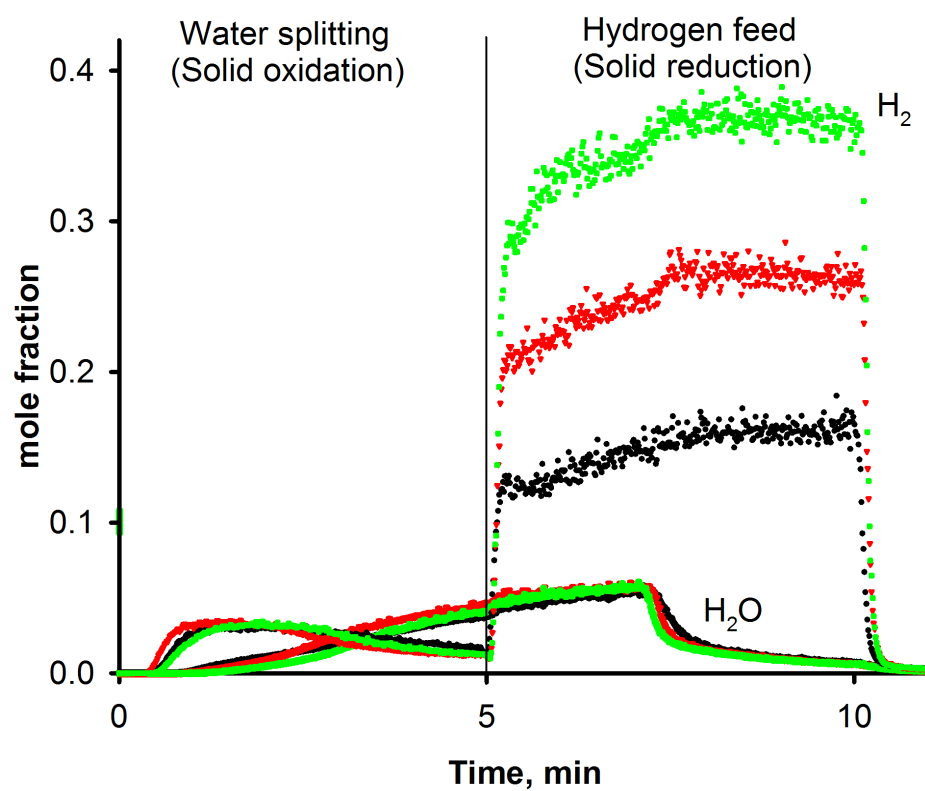


Figure 6.12 Water vapour-hydrogen cycles at 847 °C at 0.04 mol/mol (4 mol%) water in the feed gas during the oxidation cycle and 0.18, 0.29, and 0.39 mol/mol (18, 29, 39 mol%) during the reduction cycle with hydrogen.

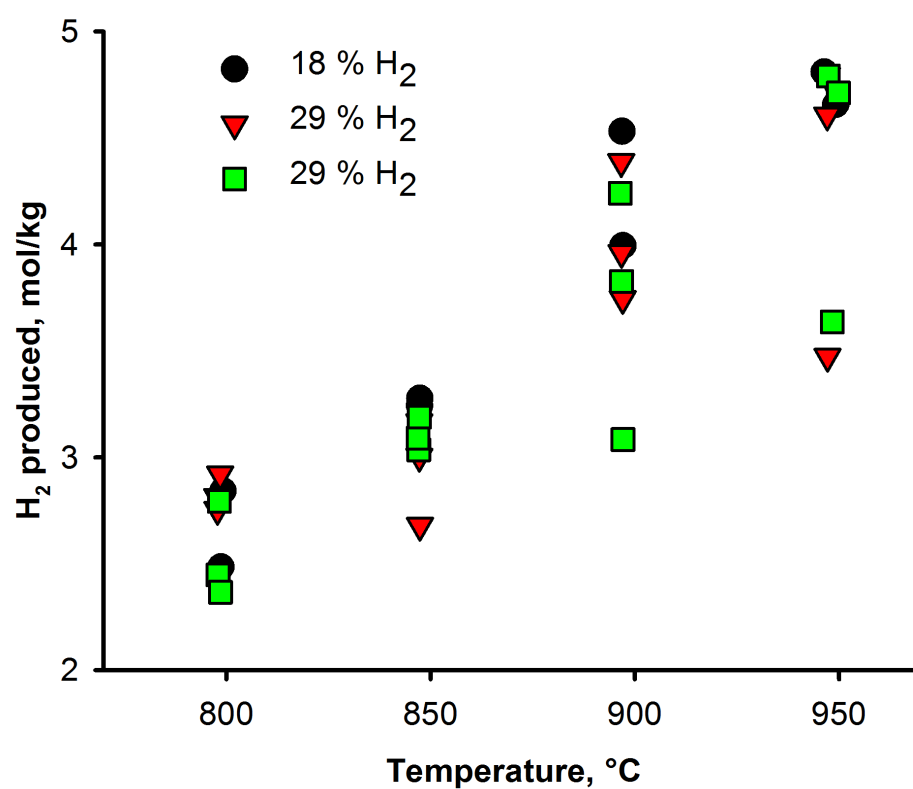


Figure 6.13 H₂ produced during water splitting cycles under 10 % H₂O between 800–950 °C.

shift reaction (Equation (6.17)), for which the enthalpy change is 48 kJ mol^{-1} of H_2 at 800°C . This thermodynamic limitation means that it is unlikely to improve the heat balance of the CLWS technology.



We compared the energy balance (per moles of metal oxide) of the CLWS to that of the CLC with a water splitter and carbon dioxide reductor (CLC/CR/WS) (Table 6.4). For this analysis, we selected copper, iron, and manganese oxides, which have been tested in chemical looping, and for which the carbon reduction and/or water splitting activities are available [64].

Table 6.4 compares the enthalpy variations at 800°C for the fuel reactor (FR) with methane (Equation (6.15)), the air reactor (AR), the water splitter (Equation (6.16)), and the carbon dioxide reductor (CR). The CLC/CR/WS configuration is less endothermic than the CLWS, and could also supply energy if iron oxides were used, provided that FeO possesses CO_2 reduction properties. Another possibility is to take advantage of the energy output of the CLC with iron oxides and add a CR/WS with reduced pyrolusite, resulting in an almost auto-thermal process (4 kJ mol^{-1}). CLC/CR/WS with copper and manganese oxide requires similar energy inputs, meaning that the selection of the metal oxide should be based on syngas production and thermal stability. For example, cuprite (the mineral form of CuO) agglomerates at high temperatures [11]. A CLC/CR/WS process with pyrolusite would produce 14 times more hydrogen than a CLWS with supported mixed Cu-Fe oxides [64].

Together with combining energy and syngas production, adding a water and carbon dioxide splitter could serve as a recycling device for spent end-of-life particles. Unfortunately, while repeated oxidation-reduction cycles activate the pyrolusite towards CO_2 splitting, they may compromise its mechanical integrity. The spent pyrolusite could be a source for the splitting

Tableau 6.4 Thermodynamic data (per mole of metal oxide) of the reactions involved in the fuel reactor with natural gas (FR), air reactor (AR), water splitter (WS), and CO_2 reductor (CR)

$\Delta H_{800^\circ\text{C}} / \text{kJ mol}^{-1}$	FR	AR	WS	CR	CLWS	CLC/CR/WS
Redox couple						
CuO/Cu	-51	-150	99	133	48	31
$\text{Fe}_3\text{O}_4/\text{FeO}$	94	-98	-47	-13	48	-63
$\text{Mn}_3\text{O}_4/\text{MnO}$	28	-76	20	54	48	26

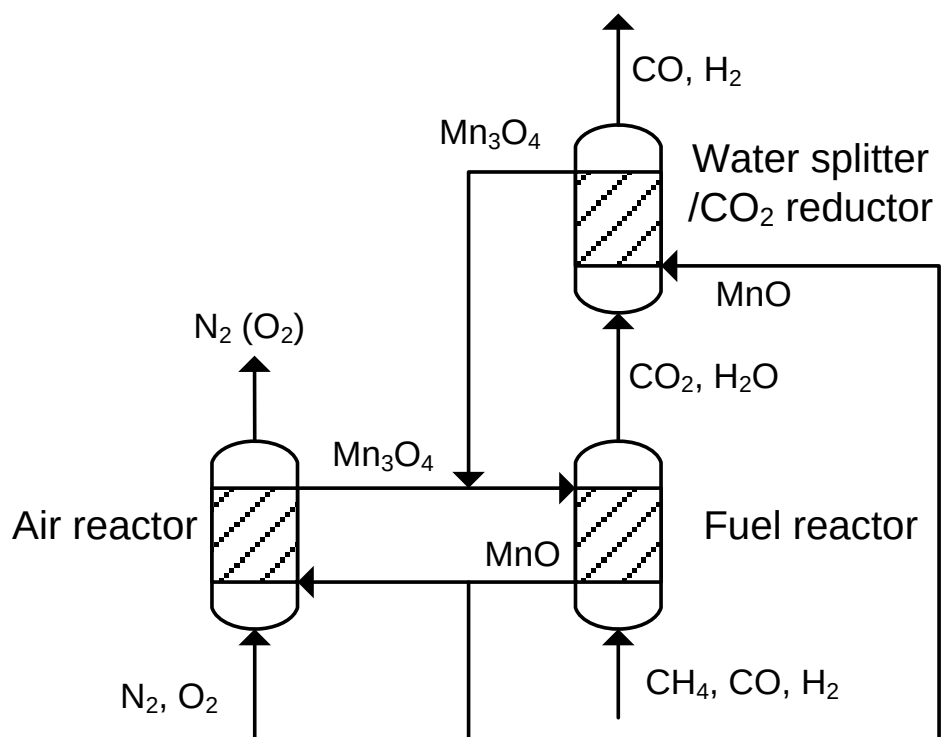


Figure 6.14 Block diagram for the chemical looping combustion process with a CO₂ reductor and water splitter.

of carbon dioxide and water. Rather than disposing of fines, they can be reconstituted (with a binder, for example) to generate CO and H₂ from the fuel effluent.

6.4 Conclusion

Producing syngas from the exhaust gas of chemical looping combustion technology (rather than sequestering CO₂) may improve CLC process economics sufficiently to warrant a full-scale demonstration plant. Pyrolusite, a manganese oxide mineral, produces syngas from carbon dioxide and water. At 960 °C the maximum CO specific production was 5,5 mol kg⁻¹, which is an order of magnitude greater than any metal oxide reported in the literature. Dosing the mineral sequentially with equal concentrations of reductant and oxidant in the same time period produced less CO than asymmetric dosing. Hydrogen productivity peaked at 4,8 mol kg⁻¹ at 947 °C, resulting in a 7,7 % transferred oxygen on a mass basis, i.e. a value equal to the theoretical value. In the water splitting experiments, no equilibrium between water and hydrogen was measured, and the reaction was much slower than the CO₂ splitting. Future studies should concentrate on co-feeding CO₂ and H₂O simultaneously rather than sequentially.

CHAPITRE 7 ARTICLE 4 : KINETICS OF CARBONATION AND DEACTIVATION OF A CALCIUM-COPPER OXIDE FOR COMBINED CHEMICAL AND CALCIUM LOOPING

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Article soumis à la revue *Chemical Engineering Journal*

Abstract

Removing carbon dioxide from industrial effluents via solid carbonate sorbents is a potential greenhouse gas mitigation strategy that can also produce hydrogen from the effluent in water gas shift reactors downstream. However, regenerate the calcium oxide (from the carbonate) requires high temperature that is provided via an oxidation step. To avoid costly oxycombustion to regenerate the CaCO_3 , it is possible to use the heat generated during the reduction of a chemical looping agent. Unfortunately, sorbents sinter thereby and consequently the surface area drops in the regeneration step. A mixed CuO-CaO sorbent with 10 % calcium aluminate binder lost 84 % of its initial BET surface area during the first 100 min on stream. Homogeneous calcium-copper-cement oxide sorbent deactivate to the 0.5 order with respect to the remaining surface area and a decay constant equal to $2,86 \text{ min}^{-1}$. An empirical equilibrium power law model characterizes the carbonation rate from 425°C to 665°C with 10 % to 20 % CO_2 in a 45 mm bubbling fluidized bed. The activation energies of the forward and reverse reaction are 220 and 120 kJ mol^{-1} , respectively. In addition to sintering, the reaction rate of the regeneration step decreases with time on stream following a zero order process. We attributed this gradual irreversibility to increased crystallinity, reducing the diffusion rate of CO_2 to the active carbonate phase. By integrating this resistance to the kinetic model, we are able to explain 99 % of the variance in the gas profiles measured by a mass spectrometer.

7.1 Introduction

The production of hydrogen, both from the commercial steam methane reforming (SMR) process and from coal gasification, relies on water-gas shift (WGS) reactors to increase the hydrogen content of the reformed gas. The hydrogen content is increased with pressure swing adsorption technology or amine scrubbing [263]. However, a loss of efficiency results due the low temperature needed for the removal of CO_2 : the gas from the WGS reactors must be

cooled from 300-400 °C to 10-40 °C for chilled ammonia and amine scrubbing, respectively [6]. The use of a CO₂ acceptor in WGS reactor, in addition to an increase process efficiency, favors the production of H₂ by removing the carbon dioxide and shifting the chemical equilibrium, as well as partially providing heat for the endothermic SMR reactions due to the exothermic carbonation reaction [263], without requiring low temperature for CO₂ removal. The resulting sorption-enhanced SMR (SE-SMR) process for hydrogen production requires a catalyst that combines nickel and calcium oxide. Ni-CaO have the additional advantage of lowering the SMR reaction to 650 °C (as opposed to 800-1000 °C in SMR) as well as increasing the hydrogen content to 99 % (dry basis) [264, 265]. Doping the sorbent with sodium also increases the absorption capacity of Li₂ZrO₃ [266].

In addition to SE-SMR, removing of carbon dioxide from industrial effluents is an alternative greenhouse gas mitigation strategy. The sorbent, e.g. lime, traps and concentrates CO₂ for storage (for its further sequestration). The calcium looping cycle (CaL) is based on the reversible reaction of lime and carbon dioxide to limestone :

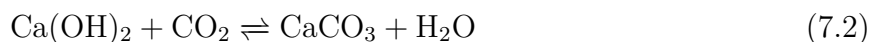


In calcium cycles, lime is regenerated from limestone with the heat provided by the reaction of pure oxygen and a fuel, to avoid diluting the CO₂ stream with nitrogen. However, if an oxycombustion reaction provides the heat, then the economics the calcium looping process suffers from the use of costly pure oxygen. As an alternative, the exothermic reduction reaction of metal oxide can provide the heat for the sorbent regeneration in the combined chemical looping combustion and calcium looping process (CLC-CaL) [267, 268]. Copper is an ideal chemical looping agent on the basis of its superior exothermic heat of reduction : the oxygen transferred as well as the heat released during the reduction of the metal oxide with methane is sufficient to regenerate the sorbent, as opposed to that of manganese oxides, the second-best choice [29]. The use of combined CaL-CLC reduces the energy penalty from 11 to 4 %, compared with amine scrubbing [269].

The cost of CaL-CLC is minimized by using economical natural limestone as the calcium looping agent. However, natural limestone deactivates during repeated calcination. Waste material can also serve as template for synthetic sorbent due to their high CaO content and low cost [270]. Additionally, due to the high CO₂ concentration during calcination, high temperatures are needed [271]. The carbonation activity decreases with cycling due to sintering (loss of surface area and porosity), as well as sulfation and ash fouling due to the formation of a CaSO₄ shell when coal combustion provides the heat for the sorbent regeneration [272] or in the presence of gas phase sulfur [273].

Two strategies can limit thermal deactivation : sorbent or process modifications. Al_2O_3 , ZrO_2 and CaZrO_3 supported calcium oxide are less prone to sintering during calcination at 950°C [84, 274]. The addition of binder such as kaolin and magnesium oxide can also limit the deactivation of natural lime while reducing its CO_2 storage capacity [275]. Tailoring the structure of the sorbent can also reduce deactivation : A hollow microspherical sorbent prepared by a sol-gel hydrothermal method maintained a higher activity after several carbonation cycles [276]. The other strategy is to modify the process conditions. Staged carbonation (carbonator operating at low CO_2 partial pressure and 650°C followed by a recarbonator – higher CO_2 pressure and 700°C to 800°C) limits deactivation by increasing the residual carbonation extent [277, 278, 279, 280]. Pressure swings can also improve the residual calcium utilization [281]. Increasing the pressure is beneficial up to approximately 0,4 MPa, a point from which its effect is negligible [282].

Limestone can also be produced from hydrated lime ($\text{Ca}(\text{OH})_2$) via indirect carbonation (Eq. 7.2). Hydrating the sorbent prior to the carbonation reaction limits deactivation, but the extent of CO_2 capture is reduced [272, 283, 284]. The addition of water in a pelletization vessel reactivates spent sorbents [285].



In addition to maintaining the carbonation extent over repeated cycles, maintaining the mechanical integrity of the sorbent is also critical. Indeed, the preferred configuration for the integrated CaL-CLC cycles is a circulating fluidized bed, in which sorbents suffer extensive attrition [268]. The attrition resistance of cadomin-based natural CO_2 sorbent, and that of a synthetic combined calcium-copper sorbent were poorer than fluid catalytic cracking (FCC) catalyst and vanadyl pyrophosphate (VPO) catalysts [286].

The CLC-CaL process relies on three reactors : carbonator, calciner/reductor and the oxidation reactor. In these combined cycles, the solid circulation sequence is challenging : copper should not be reduced in the gasifier/carbonator in order to provide the heat to regenerate the lime, or the heat release during the oxidation of copper should not initiate the calcination reaction (which would lead to the emission of CO_2 in the air reactor) [268]. Carbonation of lime should be preceded by oxidation of copper in the case of homogeneous Ca-Cu oxides to ensure that copper sites are not blocked by the CaCO_3 phase [268]. Copper oxide reduction kinetics are faster than that of limestone calcination. However, the limestone calcination and copper oxide reduction kinetics can be matched (i.e. lowering the fast copper reduction kinetics to match the limestone decomposition rate) by adding steam in the calciner/reductor [182]. Adding Mg also increases the CO_2 uptake and minimizes coking during reduction [287].

Besides calcium-based sorbents, magnesium-rich minerals can also fix CO_2 as carbonates at low temperature. Mg_2SiO_4 converts up to $0,05 \text{ g g}^{-1}$ of CO_2 (first carbonation) to magnesium carbonates between 100°C to 200°C . An empirical power law model characterized the carbonation kinetics, with an activation energy of 43 kJ mol^{-1} [288]. Fagerlund et al. [289] measured a 7 times faster carbonation reaction rate of $\text{Mg}(\text{OH})_2$ in a pressurized fluidized bed over MgO in a pressured TGA operated at 300°C and 20 bar. They measured up to 60 % MgCO_3 conversion between 370°C to 540°C and from 1 bar to 45 bar. The maximum carbonation extent was at 510°C and 40 bar.

7.1.1 Kinetic characterization

Carbonation Carbonation occurs at a fast initial rate, followed by a slower second stage corresponding to CO_2 diffusion through the newly formed carbonate layer after approximately 20 min (high carbonation extent) [290, 291, 292]. Both grain [281, 293, 294, 295] and pore models [296, 279] explain the kinetics of carbonation via a pore filling process. Sulfation kinetics was also modeled using a random pore model with limited success [297]. The measurements of the evolution of the pore volume with the extent of carbonation validated the pore model : it decreases linearly with the extent of carbonation (50 % reduction for a 65 % carbonation), with a negligible temperature effect [15]. The grain model consists of a shrinking core mode applied to single grains for the initial fast reaction controlled regime, followed by a Ginstling-Brounshtein model for the diffusion regime. The diffusion regime starts when the CaCO_3 reaches a critical thickness of 50 nm, corresponding to 5 min reaction time at 650°C under pure CO_2 [298]. The carbonation reaction mechanism has also been described with a combination of pore filling when limestone forms on the defects of the crystal structure (e.g. grain boundaries), and sintering caused by the high temperature, leading to grain enlargement and pore coarsening [299, 281]. These models adequately characterize the initial fast reaction, but fail to describe the slower diffusion-related second stage. Rouchon et al. [300] succeeded in describing both stages with the concept of separable reactivity : the kinetics of the reaction is modeled using the product of a geometrical function describing the evolution of the morphology and a reactivity function (similar to classical mechanistic rate expressions).

The carbonation reaction is first order with respect to CO_2 concentration, until reaching the equilibrium partial pressure. CaO catalyzes the water-gas shift reaction. Adding syngas and steam in the CO_2 stream doubles the apparent carbonation activation energy [295]. Carbonation proceeds via the formation of a surface complex (Eq. 7.3), which forms limestone (Eq. 7.4) [295]. The further conversion of the surface complex into calcium carbonate is fast

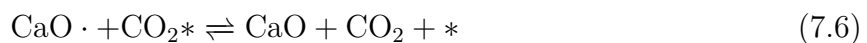
at low CO_2 partial pressure, and has no effect on the kinetics of the reaction [301]. At high pressure, some authors have reported that the kinetics is proportional to the intermediate $\text{CaO} \cdot \text{CO}_2$ species [282].



The vast majority of the kinetic models for the carbonation reaction were from TGA data. Instrument dependent effects (e.g. extensive sintering due to the high power density of TGAs) and mass transfer limitations can lead to erroneous kinetic parameters [302].

Sorbent regeneration The kinetics of the limestone calcination under low CO_2 partial pressure has been extensively characterized with morphological models applied to data obtained in TGA [182]. However, the kinetics of repeated carbonation/calcination cycles is less covered in the literature. The calculated activation energy varies from 90 kJ mol^{-1} to 170 kJ mol^{-1} depending on the model and origin of the sample (shrinking core [303] and grain models [304]). The Prout-Tompkins nucleation model characterized the regeneration kinetics from 857°C to 895°C at CO_2 partial pressures greater than 50 % [271].

Limestone decomposes to lime and forms an intermediate metastable $\text{CaO} \cdot$ phase [271]. The two step mechanism involves the decomposition of limestone and the desorption of carbon dioxide (Eq. 7.5 and 7.6).



In this paper, we model both the deactivation and the carbonation kinetics of a homogeneous calcium-copper-cement combined carbonate and chemical looping agent.

7.2 Material and methods

CanMET Energy prepared a homogeneous calcium and copper oxide sorbent by wet mechanical mixing followed by extrusion and calcination [268, 29, 285]. The sorbent is composed

of 40 % calcium, 50 % copper and 10 % of a calcium aluminate-based cement binder to improve attrition resistance and to stabilize the morphology [29]. The sorbent has a particle size between 250 μm to 600 μm , with a 400 μm Sauter diameter (Horiba LA 950 Particle size analyzer). The sorbent consists of large CuO-rich grains, and smaller CaO grains [29]. The sorbent has a bulk density of 1,2 g cm^{-3} (Scott Volumeter) and a particle density of 3,20 g cm^{-3} (Micromeritic gas pycnometer). Its minimum fluidization velocity is 20 cm s^{-1} at ambient conditions and 8,2 cm s^{-1} (NTP) at 600 °C. The sorbent has an initial BET surface area of 23,3 $\text{m}^2 \text{g}^{-1}$, pore volume of 0,14 $\text{cm}^3 \text{g}^{-1}$ and an average pore radius of 15,3 Å, calculated with the Barrett, Joyner et Halenda (BJH) method.

We loaded 105 g in a 45 mmID quartz tube, corresponding to a 56 mm bed. The bed is 700 mm long, followed by a 70 mmOD 200 mm long disengagement section (Figure 7.1). For both the carbonation and regeneration reactions, Bronkhorst mass flow controllers maintained the gas flowrate so that the superficial gas velocity was 5 cm s^{-1} (NTP). We carbonated the sorbent for 5 min with a CO_2 mole fraction from 5 % to 20 % and temperature between 460 °C to 600 °C, then calcined under Ar up to 900 °C at a 20 °C min^{-1} , or until the CO_2 concentration dropped to zero. An Omnistar Pfeiffer quadrupole mass spectrometer monitored the gas composition. We sampled 1 g to 2 g of sorbent from the bed before and after the first 6 carbonation cycles (first 5 calcination cycles), as well as after the 15th carbonation and calcination and measured the evolution of the BET specific surface, average pore volume and pore radius of the samples to characterize the deactivation of the sorbent.

We modeled the hydrodynamics of the bubbling fluidized bed as a plug flow with axial dispersion (D_z) for the gas phase and a completely stirred tank reactor (CSTR) for the solids. We neglected the effect of the bubbles in the bed : the gas concentration after a step change in the inlet composition at ambient temperature monotonically increased without the characteristic disturbances in the MS signal attributable to a bypass of unreacted gas. By assuming a CSTR for the solids, we neglected the presence of a traveling reaction front through the bed (e.g. in the case of fixed beds).

In the absence of an inert tracer with the CO_2 fed to the reactor, we estimated the axial dispersion coefficient based on the response of the exit gas concentration to a negative concentration step change to the inlet gas composition (washout). We validated this approach at ambient conditions : the axial dispersion coefficient calculated with the washout function characterized the positive step change in the inlet concentration. We calculated the axial dispersion coefficient by curve fitting of the washout function with D_z as a parameter. The resulting value was $6,6 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ at reaction conditions.

The temperature was considered uniform over the bed height since we collected the process

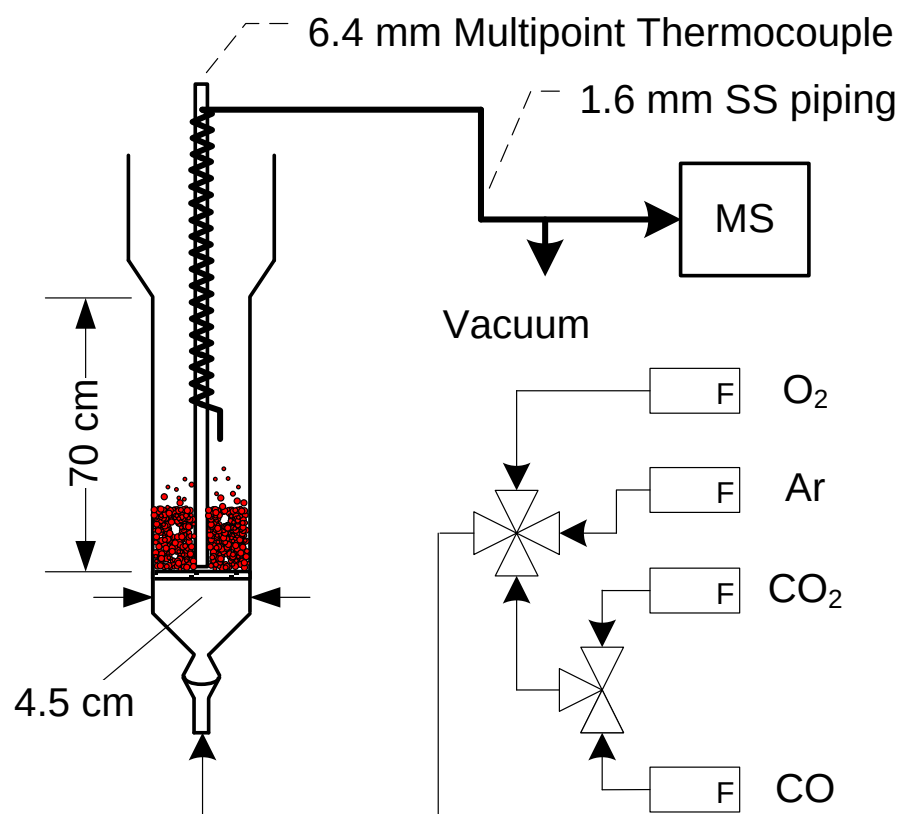


Figure 7.1 45 mmID fluidized bed reactor to sequentially reduce and oxidize the homogeneous Ca-Cu-Argon purges the reactor after each oxidation and reduction step.

gases at 8 cm above the bed, i.e. in the hot reaction zone : The MS was connected to a 1,6 mmID stainless steel tube with its inlet positioned over the bed and its other end connected to both MS and vacuum (Figure 7.1).

7.3 Results and discussion

Deactivation

After heating up to 500 °C under a steady flow of air (50 min ramp), the initial 23 m² g⁻¹ BET area dropped to 12 m² g⁻¹. Then, during the following 16 carbonation-calcination cycles (corresponding to 33 h on stream, including an overnight idle period at 570 °C under a steady flow of Ar), the specific surface decreased rapidly and stabilized at 2,3 m² g⁻¹ (Figure 7.2). After the first 5 min carbonation at 500 °C (corresponding to a mass increase of 7,5 g g⁻¹ of CO₂ per mass of sorbent), the BET area dropped to 5,0 m² g⁻¹. The subsequent calcination lead to a slight decrease in specific area, followed by an increase during the second carbonation : the BET area increased to a slightly higher value than that corresponding to the first carbonation, even though this second carbonation occurred at only 425 °C and yielded a 1 % mass increase. During the following cycles, the carbonated and calcined BET area were identical, until the fifth carbonation, where the tendency reverts with higher calcined BET surface compared to the carbonated state. This agrees with previous assertions that calcination increases the surface area due to the non-porous nature of calcium carbonate [290]. However, changes in BET surface area are only evident at large extent of reaction : the specific BET surface area remained constant from 0 % to 40 % extent of carbonation, then decreased by 63 % for the remaining 30 % [15].

Sintering can explain the decreasing trend of the combined carbonated-calcined state of the sorbent. We modeled the evolution of the BET surface using the generalized power law equation (GPLe, equation 7.7) [194], where S represents a time dependent normalized surface parameter (with its initial, S_0 , and residual value, S_r), taken as a measure of the activity ($a(t)$) of the catalyst. We were able to explain 93 % of the variance in the BET data with a 0.5 reaction order and a 2,86 min⁻¹ decay constant GPLe (Figure 7.3).

$$-\frac{d(S/S_0)}{dt} = k_d \left(\frac{S}{S_0} - \frac{S_r}{S_0} \right)^m \quad (7.7)$$

The difference in BET area after carbonation and calcination is less straightforward to explain. Manovic and Anthony [299] proposed a pore-skeleton model based on mass variations analysis during carbonation and calcination of natural limestone. They suggested the pre-

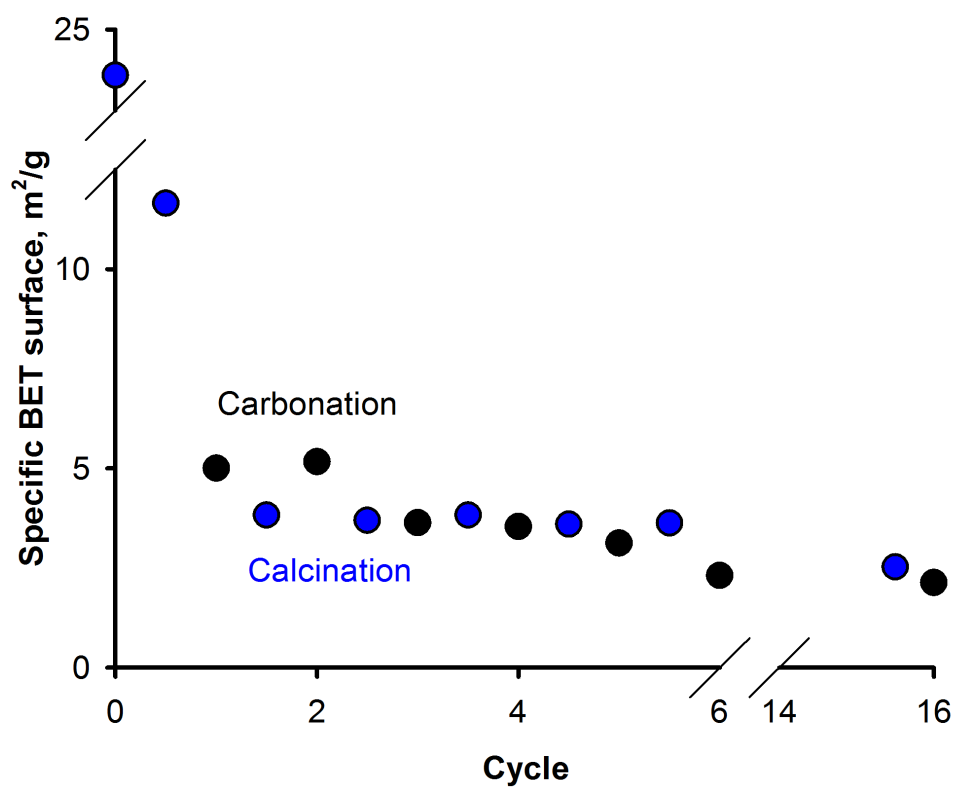


Figure 7.2 Evolution of the specific BET surface at the end of the carbonation and calcination cycles.

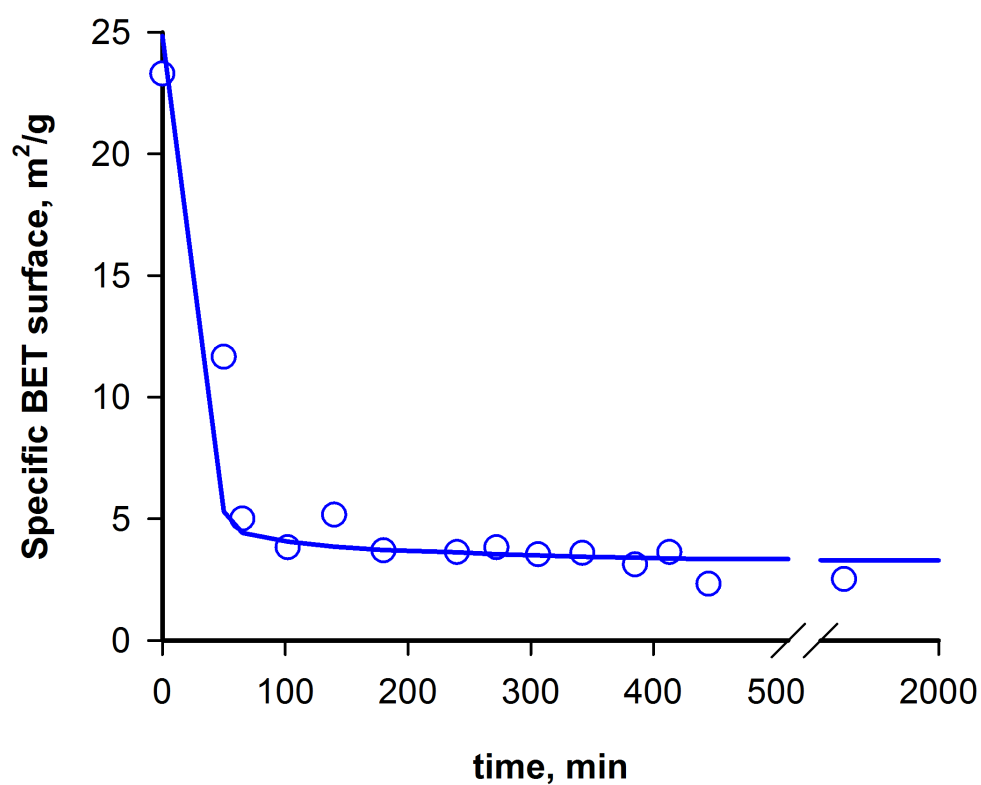


Figure 7.3 Evolution of the specific BET surface modeled with a 0.5 reaction order and 2.86 min^{-1} decay constant generalized power law equation.

sence of an external soft skeleton responsible and a internal stable unreacting core that serves to protect the particle morphology. Their model predicts the formation of larger pores with increasing cycles, and a decrease in surface resulting in a decreasing activity. However, we measured a decreasing carbonated pore volume with increasing cycles, and an increased calcined average pore volume (Figure 7.4). Assuming that carbonation is a pore filling process, the gradual loss of activity can be attributed to a combination of sintering (loss of BET area) and irreversible carbonation (decrease in pore volume over time).

In fact, the sorbent acquires a residual extent of carbonation over time, that can be regenerated only for extended calcination : We measured a maximal extent of carbonation after having left the sorbent under an argon flow at 570 °C for 24 h (idle). During the first carbonation cycle at 590 °C after the extended idle period, we measured a carbonation extent of 0,03 g g⁻¹ of CO₂ per initial mass of oxide, corresponding to 134 % that measured during continuous measurements at the same temperature. Complete regeneration would thus be a kinetic process : extended calcination leading to maximally regenerated sample. The measured average pore radius varied almost randomly with no defined tendency, aside from a higher value for the carbonated state.

Carbonation

The extent of carbonation equals the mass of CO₂ uptake divided by the total mass of the sorbent by calculating the area under the curve of the gas profile, times the total concentration, and subtracted the total CO₂ concentration fed to the reactor. We corrected the superficial gas velocity using the gas law and a mole balance on the argon to account for the change in number of moles (removal of one mole of CO₂). The carbonation extent per mass of oxide is almost constant from 410 °C to 515 °C, then linearly increases up to 660 °C, peaking at 4,3 % (Figure 7.5), which compares with that of other researchers (e.g. 7,6 % for 20 min carbonation at 750 °C [305]). The same CuO-CaO sorbent trapped up to 0,07 g g⁻¹ during 20 min carbonation [306], i.e. less than that of biomass-templated sorbents (0,24 g g⁻¹ on a mass basis) [270]. The carbonation extent abruptly decreases above 665 °C, and the calculation of the CO₂ uptake is impractical due to the equilibrium of the forward and reverse reaction, i.e. the combination of the washout of the CO₂ in the reactor volume, and the emission of CO₂ from the calcination of the sorbent.

The gas profiles at minimum, intermediate and maximum carbonation extent temperatures (corresponding to 550, 614 and 665 °C, respectively) qualitatively highlight the reaction scheme (Figure 7.6). The observed reaction appears to involve four elementary steps : i) an initial induction period characterized by a rapid increase of the unreacted CO₂ flowing

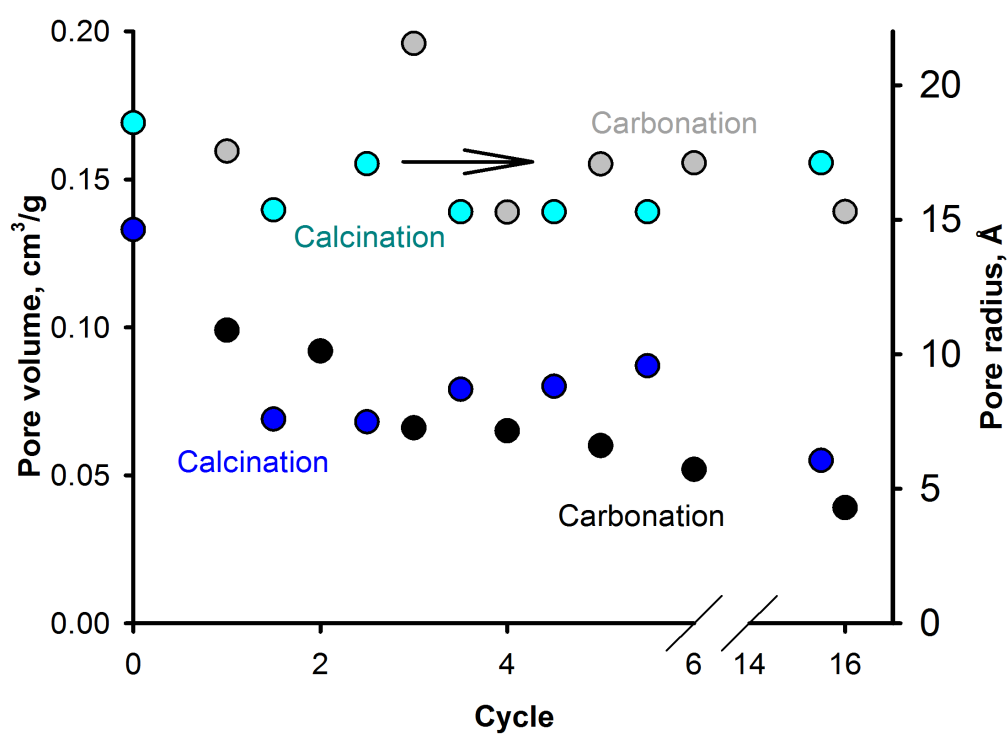


Figure 7.4 Evolution of the average pore volume and radius at the end of the carbonation and calcination cycles.

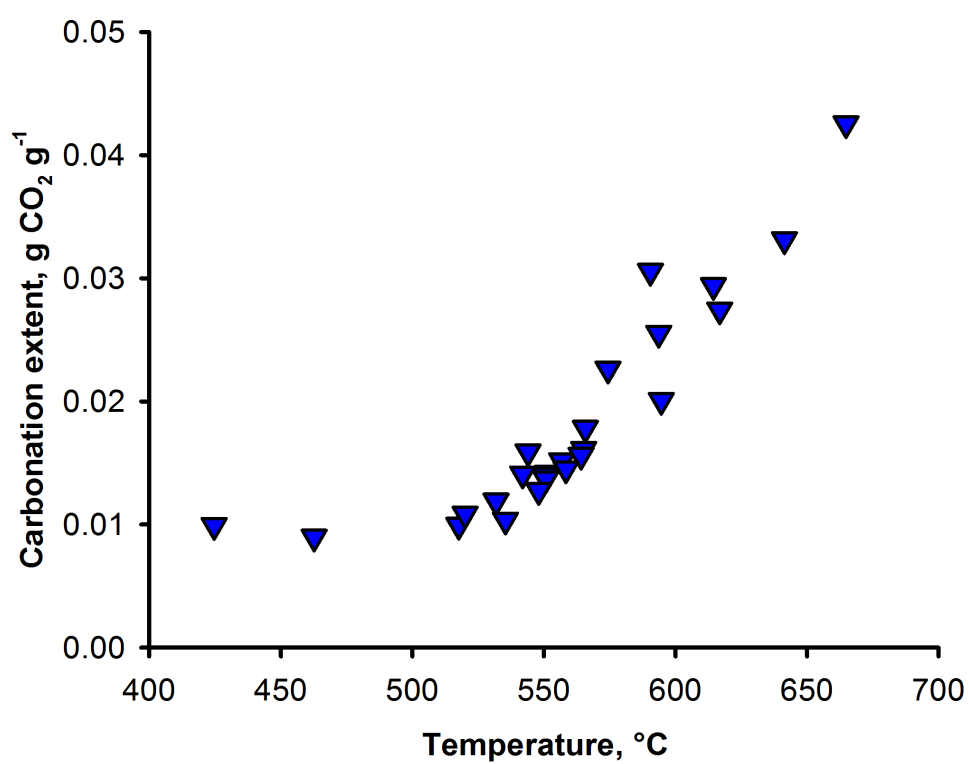


Figure 7.5 Extent of carbonation as a function of the carbonation temperature.

through the reactor ; ii) a fast carbonation regime (gently increasing CO_2) followed by a iii) slower step (steep CO_2 slope), and iv) a final fourth mechanism with almost constant CO_2 uptake (slowly increasing CO_2 until reaching the inlet concentration). Other researchers observed the induction period, but at very different time scales (up to 20 min) [15, 292]. The fast carbonation is characterized by a rapid CO_2 consumption for 20 s, suggesting a surface reaction. The reaction then shifts to a slower CO_2 uptake associated with the combination of diffusion and reaction in the bulk, with diffusion controlling the kinetics.

The surface site density can also be extracted from the gas profiles, if we can assume that the surface reaction rate is faster than diffusion. At 665°C , a single step dominates (constant CO_2 uptake). We can assume that the diffusion resistance can be neglected at this temperature. At 552 and 614°C , there is a change of slope at approximately 30 s, which corresponds to the end of the initial fast surface-related carbonation regime. We also observe that the slopes of the gas profiles at 614 and 665°C are identical ($0,03 \text{ mol m}^{-3} \text{ s}^{-1}$). We calculated the specific total CO_2 uptake corresponding to this surface reaction, divided by the BET surface area, and obtained a surface site density of $8,3 \times 10^{-4} \text{ mol m}^{-2}$. We used this value to fit the data throughout.

We derived the reaction rate by considering the state of the surface : when carbonation starts, the CO_2 molecule can collide with cement, CuO , CaO and partially carbonated CaO , with a probability proportional to the area covered by the four phases. Assuming that the surface can be estimated from the bulk composition, the surface area of exposed CaO is proportional to its volume fraction. We also assumed that elastic collisions occur between CO_2 and CuO as well as the cement aluminate, and neglected possible diffusion. We derived the reaction rate by applying the law of mass action to the surface reaction :



To account for the conversion of CaO into CaCO_3 , we assumed that the surface conversion could be approximated by the bulk solid conversion α . The result is a reaction rate that can be expressed a function of the solid conversion, the CO_2 partial pressure, the surface site density N_s , and the volume fraction of CaO and CaCO_3 (Equation 7.9), along with the mole balance on the gas phase CO_2 and solid conversion (Equation 7.11 and 7.12), where ρ_p , ρ_{CaO} , and ρ_{CaCO_3} represent the skeletal densities of the particles, the pure CaO and CaCO_3 phases, respectively. The numerical value of the CaO volume fraction is almost identical to its mass fraction (Equation 7.10 yields a 0.38 value, very close to X_{CaO}^0 , the initial mass fraction of CaO , i.e. 40 %).

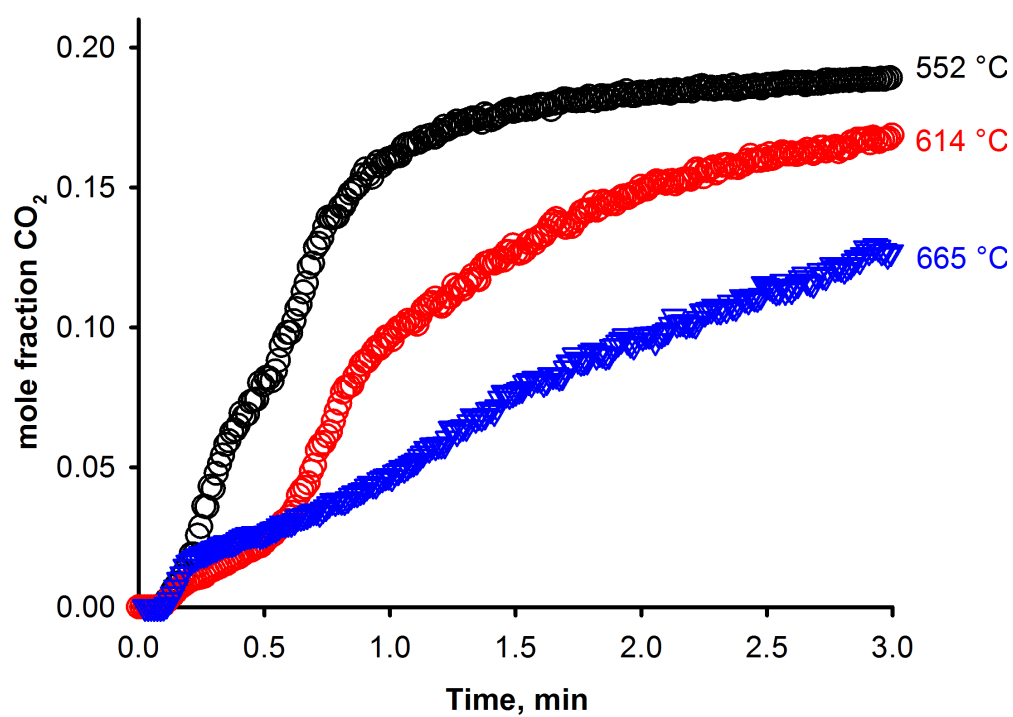


Figure 7.6 CO₂ profiles during carbonation of a gas stream containing 20 % CO₂ at 552, 614, and 665 °C.

$$r_1 = k_1 P_{\text{CO}_2} N_s \frac{v_{\text{CaO}}}{v_{\text{tot}}} (1 - \alpha) - k_{-1} N_s \frac{v_{\text{CaO}}}{v_{\text{tot}}} \frac{\rho_{\text{CaO}}}{\rho_{\text{CaCO}_3}} \frac{M_{\text{CaCO}_3}}{M_{\text{CaO}}} \alpha \quad (7.9)$$

$$\frac{v_{\text{CaO}}}{v_{\text{tot}}} = \frac{X_{\text{CaO}}^0 \rho_p}{\rho_{\text{CaO}}} \quad (7.10)$$

$$\frac{\partial C_{i,\text{CO}_2}}{\partial t} = -\frac{\partial(u_z C_{i,\text{CO}_2})}{\partial z} + D_z \frac{\partial^2 C_{i,\text{CO}_2}}{\partial z^2} + \frac{(1 - \epsilon)}{\epsilon} (-r_1) \quad (7.11)$$

$$-\frac{\partial(C_{\text{CaO}}^0 \alpha)}{\partial t} = -r_1 \quad (7.12)$$

We neglected the CO_2 equilibrium concentration due to its low value in the 425 °C to 665 °C temperature range (1×10^{-3} kPa to 2 kPa). Interestingly, by lumping all the parameters into the kinetic constants for this reversible reaction, the model is equivalent to an empirical power law, and is sufficient to fit the data of the first carbonation cycles (i.e. before the extended idle time in the reactor) performed with 20 % CO_2 from 425 °C to 600 °C (Figure 7.7). The model explains more than 97 % of the variance in the data, and the computed activation energies for the forward and reverse reaction are 220 and 120 kJ mol⁻¹.

However, when applying the empirical model to the data corresponding to the carbonation cycles after having left the sample overnight at 570 °C, it overestimates the CO_2 uptake, i.e. predicts a lower than measured CO_2 concentration. The source of this sudden change in carbonation extent cannot be explained by changes in BET surface or average pore size radius and/or volume. Considering that a commercial operation could involve extended idle time, using the kinetics of freshly used sample, as typically reported in the literature, could result in an undersized reactor.

A 10-fold drop of the surface site density after the idle period improved the fit. We supposed that the extended idle time increased the crystallinity of the CaO phase, rendering diffusion in the newly formed carbonate more difficult. Increased crystallinity is known to be detrimental in the reduction of ilmenite by CO [141] and photoreduction of cerium oxide [307]. We integrated this diffusion resistance in the model, applying it to both the forward and reverse kinetic constants, as well as the surface site density. Both resistances were correlated with the reverse resistance 1.3 times that of the forward. This result agrees with our previous observation of the gradual irreversibility of the regeneration of the calcium oxide with time on stream, corresponding to a residual extent of carbonation. The resulting kinetic model (with a zero order for the kinetic slowdown) improved the fit from 96 % to 99 % of the variance in the data (Figure 7.8), with the addition of only one parameter (resistance of the surface

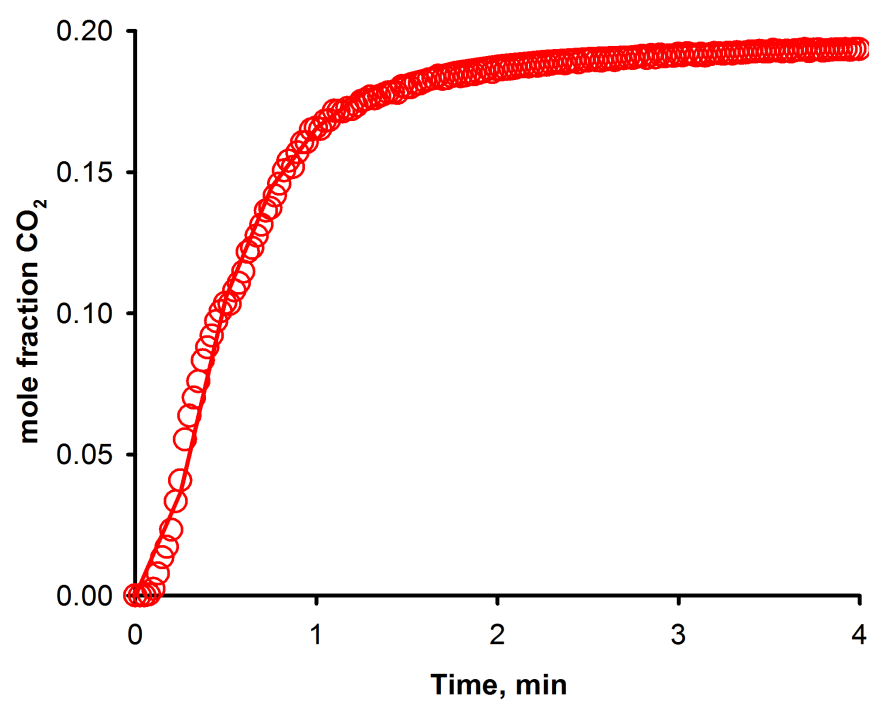


Figure 7.7 Carbonation kinetic model at 532 °C under 20 % CO₂.

reaction).

7.4 Conclusion

The design of reactors should be based on kinetic models obtained with aged catalysts (after hundreds of cycle), and not from data obtained with apparently stabilized particles (typically 10-15 cycles). Unexpected results could arise otherwise : catalysts in general should not be treated like dead objects with a fixed structure in time [308]. Undersized reactors would be designed in cases like the one reported in this article. We measured a decrease in the rate of carbonation after an extended idle time at 570 °C. The reaction rate dropped while the BET surface area, pore volume and average pore radius remained constant. We attributed the resistance to an increased crystallinity, affecting both the surface and the diffusion reaction. Similar conclusions were drawn by other researchers. Increased crystallinity is known to be detrimental to the reduction of metal oxides reduction [141, 307]. The kinetic constants for the forward (carbonation) and reverse reaction (regeneration) dropped to 11 and 15 % of their initial values, respectively, after an additional 500 min time on stream following the extended idle period. Similarly, the design of reactors based on kinetic models derived with fresh catalysts could lead to unexpected results : solids can acquire distinct catalytic properties with time on stream. In addition to numerous report on the loss of catalytic activity due to deactivation by coking, catalysts sometimes favorably evolve with time. Manganese oxide minerals become capable of reducing carbon dioxide with increasing number of redox cycles [141].

The performance of the CO₂ sorbent is crucial to both hydrogen production in water-gas shift reactors, as well as for combined chemical and calcium looping cycles. We measured carbon capture of up to 0,043 g g⁻¹ of CO₂ per initial mass of a homogeneous calcium-copper oxide between 425 °C to 665 °C under 20 % CO₂ for 5 min in a 45 mm bubbling fluidized bed. We modeled the deactivation of the sorbent by sintering during the first carbonation-calcination cycles with a 0.5 order and 2,86 min⁻¹ decay constant power law. The CO₂ sorbent loses 84 % of its initial BET surface in only 4 carbonation-calcination cycles, corresponding to 100 min on stream. In the next 2000 min, BET surface drops only from 84 % to 90 % of its initial value. An empirical equilibrium power law model describes the CaO carbonation kinetics between 425 °C and 670 °C, and from 5 % to 20 % CO₂). The model accounts for 99 % of the variance in the data, with activation energies of 220 and 120 kJ mol⁻¹ for the forward and reverse reactions, respectively.

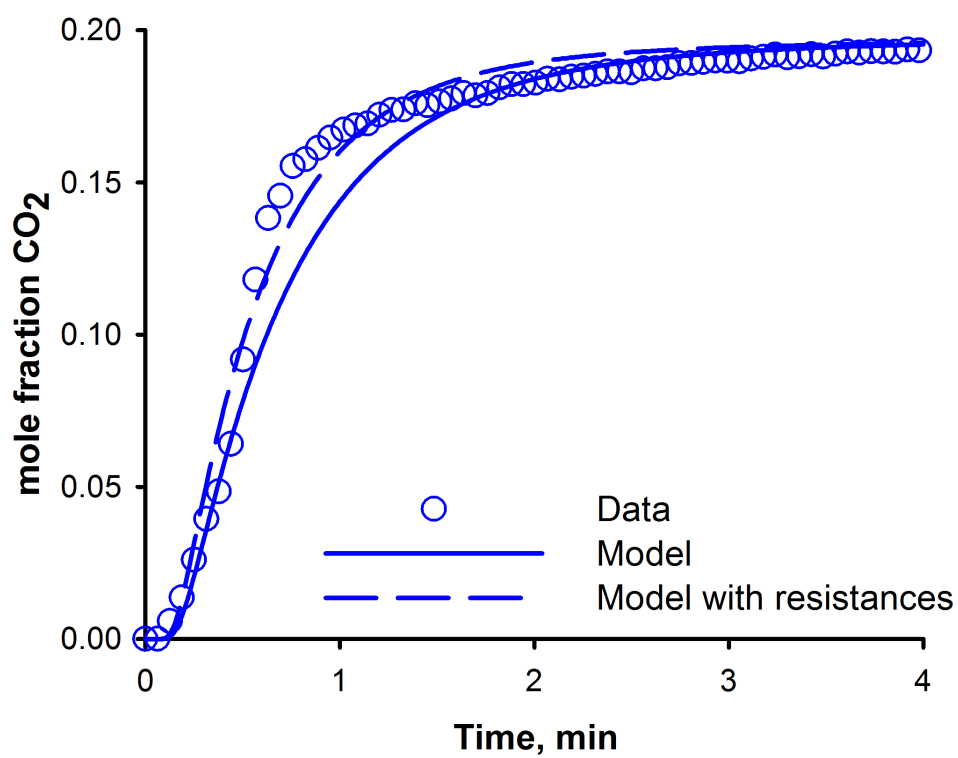


Figure 7.8 Comparison of the kinetic model with and without the zero order kinetic slowdown for a carbonation cycles at 550 °C under 20 % CO₂.

CHAPITRE 8 DISCUSSION GÉNÉRALE

8.1 Modélisation de la densité surfacique des sites actifs d'oxydes métalliques d'origines minérales

La densité surfacique de sites actifs représente la mesure du nombre de moles d'atomes d'oxygène en position surfacique dans le cas de la réduction d'oxydes métalliques, divisé par la surface spécifique. Or, alors que la mesure de la surface spécifique est rendue aisée par la technique de Théorie de Brunauer, Emmett et Teller (BET), celle du nombre d'atomes d'oxygène en position surfacique est indirecte, et toutes les mesures par des méthodes physiques tentées (Spectroscopie photoélectronique à rayons X (*X-ray photoelectron spectroscopy*) (XPS), Analyse dispersive en énergie (*Energy-dispersive X-ray spectroscopy*) (EDS) sur micrographies Microscopie à balayage électronique (*Scanning electron microscopy*) (SEM)) se sont avérées inconcluantes. La contamination de la surface des oxydes par des hydrocarbures contenus dans l'air ne permet pas d'identifier sur la base de son spectre d'émission l'ensemble des atomes oxygène en surface en XPS. De plus, cette méthode donne un comptage du nombre d'atomes sur une surface donnée. Malheureusement, le comptage provient d'une analyse du spectre d'émission de photons émis, lui-même dominé par les couches atomiques dans le volume (*bulk*) du solide. Il y a donc confusion entre les éléments du volume et ceux de la surface. Wachs et Routray [26] ont résumé les difficultés associées à l'obtention des paramètres de surface à l'aide des techniques physiques.

En ce qui concerne l'utilisation de sondes chimiques, cette méthode s'avère encore plus ardue. Pour obtenir une mesure représentative des conditions dans lesquelles l'expérience est menée, les conditions de caractérisation devraient être identiques aux conditions expérimentales, et la sonde devrait aussi correspondre (cas idéal) au réactif. Or, dans le cas de la réduction d'oxydes métalliques à haute température, la structure même de l'oxyde est dynamique et les atomes ne sont pas fixes à une position donnée. Lorsqu'un atome d'oxygène en surface est entraîné par le réducteur, il est graduellement remplacé par un autre en provenance du réseau cristallin. Aussi, la sonde chimique peut également diffuser dans les couches superficielles du solides, surestimant du même coup la densité surfacique de sites. Les méthodes de titration gaz-solide sont donc difficilement applicables à haute température, et l'effort et le temps nécessaires ne valent peut être pas la peine en raison de la faible précision des résultats (p.ex. lecture d'une faible volume de méthane produit dans une burette à gaz selon la méthode de Tamura [25]).

Nous nous sommes donc tournés sur la modélisation en guise de méthode d'estimation. Nous

avons d'abord opté pour obtenir la valeur numérique de densité surfacique de sites actifs par ajustement (paramètre, voir chapitre 4 et 6). Les valeurs numériques obtenues dans le cas de l'ilménite préoxydée oscillent entre 10 et $23 \mu\text{mol m}^{-2}$, soit du même ordre de grandeur que celles publiées pour des oxydes métalliques vrac (*bulk*), mais de nature différente [26, 25], ce qui tend à valider notre approche. De même, le profil de valeur obtenu en fonction du cycle de réduction concorde avec la tendance au frittage de l'ilménite (Figure 4.8). En effet, l'ilménite préoxydée ou non a tendance à s'agglomérer par frittage que ce soit lors de la préoxydation initiale (longue durée) ou lors des courtes périodes de réductions (entre 2 et 5 min) [11]. En ce qui concerne la pyrolusite, la densité surfacique de site actif ajustée varie entre 100 et $800 \mu\text{mol m}^{-2}$ (Figure 6.8). Ces valeurs sont jusqu'à 500 fois supérieures à celles publiées par Wachs and Routray[26] (adsorption de méthanol sur du MnO pur), et 35 supérieures à celles mesurées par Tamura et al. [25] (réaction des sites oxygène surfaciques hydratés d'un oxyde de manganèse avec un réactif de Grignard). Bien évidemment, la nature minérale de la pyrolusite (grande concentration de défauts et donc accès à un plus grand nombre de sites) peut expliquer une partie de la différence, tout comme la nature chimique différente (MnO de synthèse et mélange de $\text{Mn}_3\text{O}_4/\text{MnO}/\text{Mn}_2\text{O}_3$, en plus des autres phases présentes) de même que la température (ambiante pour Tamura, 100°C pour Wachs et de 800 à 1000°C dans nos expériences). Finalement, l'effet de la répétition des cycles d'oxydoréduction (plus de 300 pour les essais avec la pyrolusite) entraîne une augmentation de porosité, et donc une augmentation du nombre de sites oxygène accessibles.

La dernière méthode de caractérisation surfacique proposée est une mesure indirecte par bilan d'oxygène transféré lors d'une réaction essentiellement surfacique. Il est en effet apparu que la réduction de la pyrolusite calcinée par le monoxyde de carbone survient à une vitesse telle que le transfert de masse externe sature la surface de molécules de CO. Le pic initial de CO_2 émis lors de la réduction est indépendant de la concentration du CO (réducteur) pour des concentrations supérieures à environ 20 % (Figure 5.14). La réduction de la pyrolusite par le CO peut être modélisée à l'aide de la somme d'une réaction de surface et d'une réoxydation de la surface par des atomes d'oxygène du réseau cristallin. Or, la réaction de réoxydation étant beaucoup plus lente que la réaction de surface, il est possible d'estimer la densité surfacique de sites actifs en calculant l'aire sous la courbe du pic initial de CO_2 divisée par la surface totale des particules formant le lit. Le pic initial est déterminé en cessant artificiellement la réaction de surface une fois la concentration maximale de CO_2 atteinte, et en appliquant un coefficient de dispersion axiale pour obtenir la partie descendante de la courbe.

Les valeurs calculées passent de 27 à $35 \mu\text{mol m}^{-2}$ pour une concentration en CO de 5 à 10 %, puis tendent vers une valeur asymptotique de $40 \mu\text{mol m}^{-2}$ pour des concentrations supérieures de CO. Cette valeur asymptotique est cette fois en accord avec les valeurs publiées

[25, 210], ou encore supérieure d'un ordre de grandeur [27]. Sur la base des comparaisons entre les valeurs publiées de densités surfaciques de sites et celles estimées par les quelques méthodes proposées, la supériorité de la mesure indirecte apparaît clairement. On peut donc conclure que l'objectif de recherche a été atteint, et qu'une nouvelle méthode d'estimation de la densité surfacique de sites est disponible.

8.2 Comparaison des cinétiques de réduction par le CO et identification de l'oxyde le plus réactif

Les coûts d'émission de CO_2 ayant considérablement chuté, il est impératif de diminuer au maximum les coûts d'exploitation du procédé CLC pour en assurer son déploiement industriel. Or, pour le moment, la tonne de CO_2 transigeait en 2015 à 10,8 \$ (7,30 €), c.-à-d. très loin du seuil de 43 \$ (29 €) justifiant les investissements dans les technologies propres [309]. Une façon directe de diminuer les coûts d'exploitation du procédé CLC est d'utiliser un porteur d'oxygène à faible coût. Nous nous sommes donc concentré sur deux minerais d'intérêt : l'ilménite, identifiée comme le solide d'origine minérale de référence, et la pyrolusite, que nous avons identifiée. La pyrolusite coûtant une fraction du prix de l'ilménite [141], il convient maintenant de comparer les vitesses de réduction, tout comme les capacités de transfert d'oxygène afin de disposer d'un critère de choix. En effet, alors que la cinétique définit le volume de réacteur à employer, la capacité de transfert d'oxygène détermine l'inventaire de solide nécessaire pour une capacité thermique de procédé souhaitée.

8.2.1 Caractérisation de la cinétique de réduction de l'ilménite secondaire pré-oxydée par le monoxyde carbone

Sur la base de l'analyse de micrographies, nous avons d'abord pu rejeter le modèle morphologique de réaction par coeur rétrécissant (*shrinking core model*), c.-à-d. le modèle cinétique publié [17, 16, 18]. Il est aussi à noter que les différences entre les énergies d'activations (entre 81 et 170 kJ mol^{-1}) et les ordres de réaction (entre 0,67 et 2) publiés constituaient un autre indice d'incohérence de ce modèle. De plus, nous avons montré que plusieurs de formes canoniques de modèles morphologiques (tous les modèles de loi de puissance, de même que tous les modèles à coeur rétrécissant) arrivaient à un ajustement adéquat, c.-à-d. avec un coefficient de corrélation supérieure à 90 %. Ce résultat nous permet de conclure qu'il ne s'agit que de modèle d'ajustement mathématique, et non de modèle cinétique adéquat. Nous avons aussi montré que le transfert de matière de la phase gazeuse vers la surface de l'oxyde gouvernait la cinétique apparente.

Une fois l'artéfact du transfert de matière enlevé, nous avons modélisé la réaction à l'aide d'une combinaison de mécanisme de consommation d'oxygène en surface, et de réoxydation de celle-ci par l'oxygène du réseau cristallin. Ce faisant, nous avons pu calculer les énergies d'activation de ces mécanismes (50 et 90 kJ mol⁻¹ respectivement), tout comme celle associée à la cinétique d'agglomération par frittage (67 kJ mol⁻¹). Nous avons également estimé la valeur de la constante cinétique de pseudo-premier ordre égale à 0,96 s⁻¹.

Nous n'avons pu appliquer ici la méthode d'estimation de la densité surfacique de sites étant donné la vitesse considérable avec laquelle la réaction de surface avait lieu. La dominance du transfert de matière sur la réaction de surface démontre qu'il est impossible de saturer celle-ci. En raison de cette caractéristique de la cinétique de réduction de l'ilménite, nous avons opté pour un ajustement de la densité surfacique de sites, résultant en des valeurs entre 10 et 23 μmol m⁻², tel que précédemment discuté.

8.2.2 Caractérisation de la cinétique de réduction de la pyrolusite calcinée par le monoxyde carbone

La réduction de la pyrolusite calcinée suit un mécanisme similaire à celui de l'ilménite, à la différence près que la réaction de surface est à l'équilibre. C'est d'ailleurs cette caractéristique qui nous a amenés à nous interroger sur la possibilité de réduire le CO₂ en CO sur la pyrolusite réduite. Le monoxyde de carbone réduit les sites oxygène de surface, puis l'oxygène du réseau cristallin comble les sites réduits en créant des lacunes d'oxygène. L'énergie d'activation de la réaction de surface s'est avérée négative, alors que celle associée à la réoxydation des sites réduits est de 55 kJ mol⁻¹, soit près de la moitié de celle de l'ilménite, dénotant une réaction plus aisée en raison de la barrière d'énergie moindre. L'énergie d'activation négative de la réaction de surface s'explique par sa réversibilité, c.-à-d. par la réduction du CO₂ sur la pyrolusite réduite, dont la cinétique augmente avec la température. Aussi, l'évaluation des valeurs numériques des critères de Mears et de Weisz-Prater nous a permis d'affirmer que la réaction n'était pas contrôlée par le transfert de matière externe ni interne.

Les molécules de CO saturent la surface, et une fois la réduction arrêtée, on mesure une concentration résiduelle de CO qui s'attardent dans les lignes du montage lors de la vidange (*washout*). Cette concentration résiduelle diminue de telle sorte qu'elle ne saurait être modélisée par le coefficient de dispersion axiale calculé lors des essais de caractérisation hydrodynamique. Nous avons pu attribuer ce phénomène à la désorption des molécules de CO une fois l'alimentation coupée. Cette caractéristique nous a permis d'estimer la densité surfacique de sites occupés par des molécules de CO à l'équilibre à la fin de la réaction.

Alors que la réaction de réduction de la pyrolusite par le CO est limitée par la saturation de

sa surface, révélant un comportement asymptotique de sa capacité de transfert d'oxygène, nous avons démontré qu'il était possible de minimalement doubler celle-ci en co-alimentant de l'hydrogène. En effet, sur la base d'un bilan d'oxygène transféré du CO vers le CO₂ seulement (c.-à-d. excluant la quantité d'eau formée par oxydation de l'hydrogène), on obtient une capacité de transfert correspondant au double de ce qu'elle est pour le CO seul. Nous avons attribuer cette hausse de la capacité de transfert d'oxygène à une augmentation de la concentration des lacunes d'oxygène dans le réseau, facilitant la diffusion autant du CO dans la matrice rendue poreuse, que celle des ions oxygène diffusant vers la surface.

8.2.3 Sélection du meilleur porteur d'oxygène

La capacité de transfert d'oxygène de la pyrolusite est supérieure pour une durée de réduction et un réducteur (CO) donnés. Elle atteint 2 % à 808 °C, peut importe la concentration de CO, alors que celle-ci n'est que de 1,2 % à 920 °C sous 25 % pour l'ilménite préoxydée (valeur maximale). Sa capacité de transfert augmente à 1,7 % sans l'étape préliminaire de préoxydation, mais alors l'ilménite fraîche agglomère très rapidement, même sous vitesse minimale de fluidisation et durée limitée de réduction.

En première approximation, on peut estimer l'inventaire de solide dans le réacteur à combustibles par unité de puissance thermique souhaitée du procédé CLC en considérant la quantité de solide nécessaire à la conversion totale du gaz, sa pureté ainsi que sa cinétique de réduction (Equation 8.1) [153]. Étant donné qu'il s'agit d'une cinétique en régime transitoire (cinétique maximale au départ de la réaction, puis diminuant jusqu'à une valeur nulle une fois la réaction terminée), nous avons considéré une cinétique de réduction moyenne (Equation 8.2). On peut également estimer l'inventaire de solide dans le réacteur d'oxydation de façon similaire. Or, la vitesse d'oxydation est très rapide pour l'ensemble des porteurs d'oxygène et on peut donc négliger la quantité de solide dans le réacteur d'oxydation par rapport à celle du réacteur à combustibles. Les cinétiques de réoxydation des deux solides étudiés dans ce document se sont révélées impossibles à modéliser : la conversion de l'oxygène alimenté est complète durant quelques secondes, même pour des temps de séjour inférieurs à 1 s et pour des concentrations d'oxygène jusqu'à 75 %. La cinétique de réoxydation est assurément contrôlée par le transfert de matière.

$$\frac{m_{MeO,FR}}{Q_{th}} = \frac{\rho_{MeO} V_r}{x_{MeO} (-r_{MeO})_{moy} \Delta H_c^\circ} \quad (8.1)$$

$$(-r_{MeO})_{moy} = \frac{\int_{t_0}^{t_f} (-r_{MeO}) dt}{\Delta t_{red}} \quad (8.2)$$

En comparant les taux moyens de réduction de l'ilménite préoxydé et celui de la pyrolusite, on obtient un inventaire de porteurs d'oxygène dans le réacteur à combustibles de 4,3 et de $0,41 \text{ t kW}^{-1}$ de puissance thermique respectivement, soit 10 fois plus de solides dans le cas de l'ilménite. On notera par contre que la quantité de pyrolusite correspond à 4 fois celle associée aux porteurs d'oxygène de synthèse à base de cuivre [153]. Étant donné que la chaleur nécessaire à la réduction est fournie par le flux de solides circulant du réacteur d'oxydation à celui de réduction, il est intéressant de vérifier que la capacité calorifique des solides est adéquate. Or, on obtient une valeur de 136,7 et de $193,2 \text{ J mol}^{-1} \text{ K}^{-1}$ pour l'ilménite et l'hausmannite à 800°C [310, 311], c.-à-d. encore une fois une valeur en faveur de la pyrolusite. Ainsi, le flux de particules de pyrolusite circulant entre les réacteur pour assurer un transfert d'énergie adéquat ne serait que de 70 % celui requis dans le cas de l'ilménite. Le seul point faible de la pyrolusite se situe au niveau de sa tenue mécanique. Des essais sur un broyeur à jet (*jet mill*) à orifice unique (vitesse de 290 m s^{-1} et température ambiante) ont permis de mesurer des taux d'attrition 4 fois supérieurs pour la pyrolusite, tout de même inférieur à ceux du catalyseur commercial vanadium-phosphore-oxygène (VPO), utilisé pour la conversion du butane en anhydride maléique [312].

Finalement, il ne saurait être question d'identifier le meilleur porteur d'oxygène sans considérer leurs coûts. Le marché des minerais de fer et titane en est un de 3,9 milliards de dollars (2,9 milliards de dollars américains) pour l'année 2012 aux États-Unis seulement, essentiellement en raison de l'utilisation de ces minerais pour la production de pigments. Les minerais de manganèse sont 95 % moins cher que ceux de fer et titane. L'ilménite d'Australie a un coût 400\$ (300\$ américains) par tonne [313]. De plus, même si la production mondiale de minerais de titane augmente d'année en année, son coût suit la même tendance, passant de 100\$ (75\$ américains) en 2010 à sa valeur actuelle de 400\$ (300\$ américains) par tonne. Au contraire, les minerais de manganèse coûtaient 5,7\$ (4,3\$ américains) par tonne en 2014, en diminution depuis 2010 [314, 313]. Les minerais de manganèse sont essentiellement utilisés en sidérurgie, ce qui représente tout de même un marché de 1,9 milliard de dollars (1,4 milliard de dollars américains) pour les États-Unis [313].

8.3 Caractérisation du potentiel de réduction du dioxyde de carbone et du clivage de l'eau de la pyrolusite

Nous avons démontré la capacité de la pyrolusite de réduire le CO_2 en CO et la vapeur d'eau en H_2 , ce qui constitue un autre avantage de celle-ci par rapport à l'ilménite comme porteur d'oxygène potentiel pour le procédé CLC. En effet, la forme réduite de la pyrolusite soumise à plusieurs cycles d'oxydoréduction acquiert graduellement la capacité de réduire le CO_2 en

CO en intégrant l'oxygène dans son réseau cristallin (c.-à-d. sans émission de O_2 en phase gazeuse lors de la réaction). Aussi, dans sa forme oxydée, la pyrolusite activée adsorbe le CO_2 sans émissions d'autres espèces, suivie d'un relargage lors d'un dosage subséquent sous oxygène. Le nombre exact de cycles nécessaire à l'activation n'a pas été validé, mais nous avons proposé un mécanisme réactionnel en nous appuyant sur une revue des interactions entre différents oxydes et le CO_2 [216]. La réaction de clivage du CO_2 procède par le biais d'atomes de potassium agissant comme activateur (*promoter*). Le potassium agit comme donneur d'électrons, activant la molécule inerte de CO_2 en $CO_2^{\delta-}$, qui est par la suite dissociée en CO et oxygène atomique qui migre dans le réseau cristallin [212]. Le mécanisme d'activation suggéré est essentiellement dû à une augmentation de la porosité des particules de pyrolusite après plusieurs cycles d'oxydoréduction, rendant ainsi accessibles les atomes de potassium (présent à près de 1 % en masse dans la pyrolusite fraîche).

La capacité de réduction du CO_2 de la pyrolusite vieillit est de 10 à 100 fois supérieure à celle des pérovskites dopées au Sr, Ce et Fe, ainsi qu'au pérovskites $Y_{0.5}Sr_{0.5}MnO_3$, pourtant identifiés comme les meilleurs dans le domaine [251, 254]. Nous avons mesurés une production spécifique de CO maximale de $5,5 \text{ mol kg}^{-1}$ à 960°C pour un temps de contact d'à peine 0,01 s. La pyrolusite réduite peut également cliver l'eau en hydrogène. Sans analyser le mécanisme réactionnel ni la cinétique, nous avons mesuré une production spécifique maximale d'hydrogène à $4,8 \text{ mol kg}^{-1}$ à 947°C , soit une valeur deux fois plus élevée que celle obtenue sur $CoFe_2O_4$ et Al_2O_3 dans le cycle dit hercynite [239].

Ces performances de clivage de l'eau et de réduction du CO_2 ouvre la porte à des innovations majeures pour le procédé CLC, et pour les procédés industriels générant des gaz de combustion en général. En effet, dans le cadre du procédé CLC, plusieurs auteurs ont proposé des modifications de façon à favoriser un extrant gazeux (production H_2 et/ou CO) au détriment de la puissance thermique, par exemple, en remplaçant le réacteur d'oxydation, source d'énergie principale en raison de l'exothermicité des réactions en jeu, par un réacteur de clivage d'eau alimenté en vapeur d'eau [60, 64]. Or, les auteurs n'ont pas non plus pris la peine d'explicitier les effets de la vaporisation de l'eau utilisée sur le bilan d'énergie. Au contraire, en ajoutant un réacteur de clivage d'eau et de réduction de CO_2 alimenté en pyrolusite vieillie, on produit de l'énergie (essentiellement dans le réacteur d'oxydation) et des gaz de synthèse simultanément, à partir d'un courant n'ayant plus aucune valeur dans le procédé. Les coûts supplémentaires résident par contre au niveau du réacteur supplémentaire, et de la circulation de solides alimentant ce dernier.

La question de la réduction de ces solides doit par contre être résolue (autrement, il ne s'agirait que d'adsorption de CO_2 à la manière du procédé combiné CaL-CLC). Une solution

consisterait à dévier une partie du flux de particules circulant entre les réacteurs d'oxydation et de réduction, contournant du même coup le réacteur d'oxydation, et constituant ainsi une boucle fermée entre les réacteurs de réduction et de clivage d'eau/réduction de CO_2 (Figure 6.14). Il faudrait ainsi prévoir une augmentation de l'inventaire de solide pour le réacteur de réduction, en fonction de la quantité de gaz de synthèse à produire.

Le réacteur de clivage d'eau/réduction de CO_2 pourrait aussi être opéré en lit fixe, sans circulation de solides. En effet, la pyrolusite acquière graduellement la capacité à cliver l'eau et réduire le CO_2 . Or, un phénomène concomitant avec l'augmentation du nombre de cycles dans un lit fluidisé circulant est celui de la dégradation des propriétés mécaniques, phénomène empiré par la multiplicité des cycles d'oxydoréduction, qui entraînent une fragilisation de structure interne des porteurs d'oxygène en raison de la différence de masse volumique du couple redox $\text{Mn}_3\text{O}_4/\text{MnO}$ (masse volumique de 4850 et de 5400 kg m^{-3} pour l'hausmannite et la manganosite, respectivement). Ainsi, pour pallier cette augmentation de la fragilité de la pyrolusite cyclée, l'utilisation d'un lit fixe permettrait une utilisation novatrice des porteurs d'oxygène en fin de vie utile. La question de la réduction des porteurs serait par contre entière, à moins de ne valoriser leur capacité de réduction du CO_2 et de l'eau qu'une seule fois. Une dernière option consisterait à synthétiser des porteurs d'oxygène à l'aide de la pyrolusite vieillie à l'aide de liants permettant une augmentation de sa tenue mécanique.

8.4 Caractérisation de la cinétique de captation de CO_2 d'un oxyde mixte de calcium (CaO) et d'un porteur d'oxygène

Manovic et Anthony [29] ont identifié l'oxyde de cuivre en tant que meilleur oxyde pour la synthèse d'un oxyde mixte pour les applications combinées de boucle chimique de cycle à carbonate. Leur choix s'est arrêté sur l'oxyde de cuivre en raison de la plus petite variation d'enthalpie (plus grande valeur négative) de celui-ci par comparaison à celle des oxydes de manganèse et de nickel. En effet, dans les applications combinées CaL-CLC, la chaleur dégagée par la réduction de l'agent responsable de la boucle chimique fournit la chaleur pour la régénération de l'oxyde de calcium. Par contre, en choisissant l'oxyde de cuivre, la particule composite résultante est sujette à l'agglomération due au faible point de fusion du cuivre [286].

Nous avons caractérisé la diminution de perte de surface spécifique d'un solide préparé par CanMET Énergie combinant absorption de CO_2 (oxyde de calcium), porteur d'oxygène (oxyde de cuivre) et liant d'aluminate de calcium pour une meilleure tenue mécanique et pour stabiliser sa morphologie. La perte de surface spécifique au cours des premiers cycles de carbonatation-calcination peut être modélisée à l'aide de l'équation généralisée de loi de

puissance d'ordre 0,5 et de constante de détérioration égale à $2,86 \text{ min}^{-1}$.

CHAPITRE 9 CONCLUSION

9.1 Synthèse des travaux

Dans le cadre de ces travaux, nous avons été en mesure de déterminer les mécanismes de réduction de l'ilménite préoxydée et de la pyrolusite, et d'en caractériser la cinétique. Les deux oxydes sont réduits par le monoxyde de carbone selon un mécanisme similaire : une réaction de surface entre les molécules de CO et les atomes d'oxygène, et une réaction de réoxydation des sites réduits par de l'oxygène en provenance du réseau cristallin. L'énergie d'activation de la réaction de surface de la pyrolusite est négative, en raison de sa réaction inverse (réduction du CO_2 en CO) qui elle augmente avec la température. La réaction de réoxydation de la surface de la pyrolusite est plus aisée en raison d'une barrière d'énergie moindre. Son énergie d'activation est de 55 kJ mol^{-1} , en comparaison avec 89 kJ mol^{-1} pour l'ilménite préoxydée, ce qui contribue à expliquer sa réactivité moindre. La cinétique de réduction, globalement plus rapide pour la pyrolusite, permet de diminuer la quantité de solide nécessaire pour une production d'énergie donnée. On peut estimer un inventaire de solides nécessaires à la conversion du combustible dans le réacteur de réduction 10 fois moindre pour la pyrolusite. De façon similaire, le taux de circulation de solide permettant de transférer l'énergie entre les réacteurs d'oxydation et de réduction est de 30 % inférieur à ce qu'il serait pour l'ilménite.

Les travaux de modélisation cinétique ont permis de constater l'intérêt de disposer d'une méthode d'estimation de la densité surfacique de sites actifs d'un catalyseur. En effet, cette quantité apparaît dans l'expression des vitesses de réaction appliquée aux réactions élémentaires de surfaces, de même que dans les bilans de matière des espèces surfaciques. Or, les méthodes existantes de mesures de ce paramètre se sont avérées inutilisables : conditions de mesure trop éloignées des conditions expérimentales et sonde chimique non adaptée. Pour pallier ces inconvénients, nous avons validé dans un premier temps l'approche d'estimation par ajustement dans le processus de modélisation, mais surtout la méthode indirecte de titration gaz solide simulée. Celle-ci permet d'estimer la densité surfacique de sites actifs à partir du pic initial de produit émis dans le cas de réactions surfaciques saturées par les réactifs en phase gazeuse. Les ordres de grandeur se sont avérés en accord avec les valeurs estimées, dans la mesure où les valeurs mesurées d'oxydes de synthèse sont comparables avec celles s'appliquant à des oxydes d'origine minérale.

Nous avons également pu constater que certaines améliorations au procédé CLC étaient possibles et souhaitables. Premièrement, il est possible de séquestrer *in situ* le dioxyde de carbone par formation de carbonates, à l'aide d'un oxyde mixte (de synthèse) combinant

du calcium et un oxyde métallique ayant une variation d'enthalpie de réduction négative (p.ex. cuivre, ou encore manganèse lorsque réduit par le CO ou H₂). L'intérêt d'un procédé combiné de cycle à calcium et combustion en boucle chimique trouve sa pertinence dans un contexte de déplacement de l'équilibre dans la réaction d'échange eau-gaz pour la production d'hydrogène.

L'inventaire de solide nécessaire pour une captation donnée de CO₂ repose sur la capacité du solide à convertir l'oxyde de calcium en carbonate, alors que le volume du réacteur dépend de la cinétique de carbonatation. Nous avons donc caractérisé un oxyde de synthèse combinant calcium, cuivre et un additif de ciment (pour la stabilisation de la morphologie du solide et une résistance améliorée à l'attrition). Nous avons mesuré des capacités de captation de CO₂ allant jusqu'à 4,3 % à 665 °C lors de cycles de carbonatation de 5 min sous 19,7 % CO₂ dans un lit fluidisé opéré en régime bullant. Aussi, nous avons modélisé la désactivation graduelle du solide lors des premiers cycles de carbonatation-calcination. Une loi de puissance d'ordre 0,5 avec une constante de détérioration de 2,86 min⁻¹ a pu expliquer la diminution progressive de la surface spécifique de l'oxyde mixte en fonction de son temps d'utilisation. La cinétique de carbonatation a pu être caractérisée à l'aide d'un modèle à l'équilibre, possédant des énergies d'activation de 218 et 121 kJ mol⁻¹ pour les réactions directe et inverse, respectivement. Une irréversibilité graduelle a également été observée avec le temps, phénomène qui s'ajoute à la désactivation thermique. Nous avons pu quantifier cette désactivation chimique à l'aide d'un modèle linéaire de perte d'activité chimique par augmentation de cristallinité. Des facteurs de ralentissement cinétique corrélés ont été appliqués tant aux constantes cinétiques des réactions directe et inverse, qu'à la densité surfacique de site estimée.

Finalement, nous avons démontré le potentiel considérable de réduction du CO₂ en CO et de clivage de la vapeur eau en H₂ de la pyrolusite réduite soumise à plusieurs cycles d'oxydoréduction. Cette capacité, de 10 à 100 fois supérieures aux valeurs publiées des meilleurs oxydes de synthèse dans le cas de la réduction du CO₂, conduirait à une amélioration notable du procédé CLC. En effet, en plus de ne pas compromettre la puissance thermique du procédé, il serait dès lors possible de générer un gaz de synthèse à partir de gaz de combustion n'ayant plus aucune valeur mis à part leur chaleur sensible, et la chaleur latente de condensation de la vapeur d'eau. Nous avons proposé un modèle cinétique d'activation des molécules de CO₂ à partir du potassium (constituant près de 1 % de la pyrolusite fraîche) agissant comme source d'électrons.

9.2 Limitations et améliorations futures

La méthode proposée de caractérisation de la densité surfacique de site ne s'applique que dans le cas où les profils de gaz se présentent sous forme d'un pic initial de saturation, et que s'il est possible de distinguer les réactions de surface des phénomènes diffusionnels, ce qui correspond à une famille restreinte de réactions chimiques. Par contre, nous avons réussi à appliquer cette méthode d'estimation à la réaction de carbonatation d'un oxyde mixte par comparaison des profils de gaz à des températures différentes : nous avons vu qu'il est possible d'identifier des réactions purement surfaciques, et même d'identifier le début et la fin de celles-ci. Des travaux futurs de formalisation de la méthode seraient très pertinents afin d'en établir sa crédibilité. Bien évidemment, des comparaisons à l'aide de mesures, même à des conditions de caractérisation éloignées des conditions expérimentales sont nécessaires pour valider sa précision, par exemple à l'aide des méthodes de Wachs et Tamura appliqués aux minerais et oxydes de synthèse testés dans ce document.

En ce qui concerne le mécanisme d'activation de la pyrolusite pour la réduction du CO_2 proposé, il ne s'appuie que sur une analyse de la littérature et de l'analyse élémentaire de la pyrolusite. En effet, il ne nous a pas été possible de confirmer la validité du mécanisme d'activation proposé par des mesures indépendantes (malgré plusieurs heures d'analyse de Diffraction à rayons X (*X-ray diffraction*) (XRD), XPS, d'analyse de micrographies, etc.). De même, le nombre exact de cycles d'oxydoréduction n'a pas été déterminé, pas plus que le seuil de porosité minimal pour activer la pyrolusite. Par contre, l'importance du phénomène a pu être confirmée par des essais répétés sur des échantillons différents. Ces questions seront assurément au coeur de mes travaux futurs.

Certaines limitations sont également apparues dans le processus de modélisation de la cinétique selon une approche mécanistique : soit la caractérisation des paramètres surfaciques. Cette voie de modélisation peut s'avérer rapidement très exigeante du point de vue de l'effort de calculs. En effet, même dans le cas de réactions entre des molécules simples comme le dioxyde de carbone ou le méthane et des surfaces tout aussi simples (ou simplifiées pour les besoins de la modélisation), le nombre d'espèces surfaciques résultant des interactions peuvent être très nombreuses, tout comme les bilans à résoudre, en particulier dans le cas de réactions transitoires comme celles étudiées ici. En guise d'exemple, la chimisorption du méthane sur un site surfacique réduit peut se transposer en de multiples bilans de matière : CH_4^* , CH_3^* et H^* , CH_2^* et H^* , etc. Pour éviter de tomber dans l'ajustement mathématique pur multiparamètres, le recours à des techniques physiques de caractérisation s'avère crucial. En fait, la solution réside dans le couplage de plusieurs méthodes de caractérisation *in situ*, appuyé par des calculs théoriques *ab initio* ou relevant de la théorie de la fonctionnelle de la

densité (*density functional theory*).

Cette approche de modélisation comporte par contre plusieurs avantages. Par exemple, ces modèles prennent racine sur des phénomènes chimiques adaptés au problème à l'étude : les équations des taux de réaction sont développées en appliquant la loi d'action de masse sur les étapes élémentaires supposées. Il n'y a que peu de risque d'utiliser des modèles hors de leur domaine de validité, comme dans le cas des modèles morphologiques. En effet, certains de ces modèles ont été développés sur la base de réaction se déroulant dans un volume, mais sont souvent utilisés pour décrire des réactions avec une composante surfacique importante. Ce désavantage de la modélisation morphologique est accentué par la disponibilité des tableaux publiés d'expressions cinétiques, de même qu'en raison de la composante mathématique simplifiée : nul besoin de résoudre des équations aux dérivées partielles, une résolution algébrique suffit.

En termes d'ingénierie, dans la mesure où ces travaux cherchent à favoriser le déploiement commercial du procédé CLC, il reste beaucoup à faire pour lever les incertitudes entourant l'utilisation de la pyrolusite comme porteur d'oxygène. Il convient en effet de caractériser les cinétiques de réduction de la pyrolusite (et de l'ilménite) par l'hydrogène, le méthane, ainsi que de valider les cinétiques proposées par des essais de réductions combinées CO-H₂, CO-CH₄, H₂-CH₄, sur des montages expérimentaux plus grands. En fait, nous avons réalisé la plupart de ces essais. Nous nous attellerons donc à caractériser la cinétique de ces réactions dans les prochains mois.

Finalement, aussi en termes d'ingénierie, il convient de s'attarder à l'analyse de la configuration optimale de procédé pour tirer avantage des importantes propriétés de réduction du CO₂ et du clivage de la vapeur d'eau. Les travaux présentés ici ne constituent qu'une base sur laquelle construire tout un pan du développement du procédé.

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