



## Pyrolusite–CO reduction kinetics

Patrice Perreault\*, Gregory-S. Patience

École Polytechnique de Montréal, Department of Chemical Engineering, C.P. 6079, Succ. Centre-Ville, Montréal, QC, Canada



### HIGHLIGHTS

- Pyrolusite is a potential oxygen carrier for CLC and CLOU.
- CO reacts with surface oxygen and reduces  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}$ .
- Lattice oxygen from the bulk diffuses to the surface.
- The oxygen surface site density is  $40 \mu\text{mol m}^{-2}$ .

### ARTICLE INFO

#### Article history:

Received 20 November 2015  
Received in revised form 4 February 2016  
Accepted 8 March 2016  
Available online 15 March 2016

#### Keywords:

Pyrolusite  
Reduction  
Kinetics  
Chemical looping  
Surface site density

### 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  $960^\circ\text{C}$ , 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  $810^\circ\text{C}$  to  $960^\circ\text{C}$ . The direct reduction of surface oxygen sites by carbon monoxide, in equilibrium with the reverse  $\text{CO}_2$  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  $910^\circ\text{C}$ , where it peaked at  $55 \mu\text{mol m}^{-2}$ , corresponding to a 70% covered surface. The estimated oxygen surface site density followed an asymptote at  $40 \mu\text{mol m}^{-2}$ , in agreement with measured values.

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## 1. Introduction

The early concepts of chemical looping evolved in diverse applications. From the initial oxy-combustion process for natural gas [1,2], solid fuels could be handled with the outbreak of Scott et al. [3]. The process was later reoriented from its initial energy-oriented goal to focus on hydrogen production via chemical looping gasification [4], reforming of coked oxygen carriers [5] or methane [6] and water splitting [7–9]. Recently, Abanades et al. [10,11] 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  $\text{CO}_2$  sorption.

In the context of current low  $\text{CO}_2$  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 [12], cement decorated copper ores to minimize their natural agglomeration tendency [13], hematite for methane [14,15] or sewage sludge combustion [16],  $\text{K}_2\text{CO}_3$ -added hematite for direct carbon combustion [17].

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 [18–20]. However, pyrolusite was tested by Leon et al. [21] as early as 2009, but rejected due to its low crushing strength. Linderholm et al. [22] 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

\* Corresponding author.

E-mail address: [patrice.perreault@polymtl.ca](mailto:patrice.perreault@polymtl.ca) (P. Perreault).

## Nomenclature

$k'_i$	kinetic constant for surface reaction $i$	$N_r$	initial concentration of oxygen in the reactor bed (mol m <sup>-3</sup> )
$k_B$	Boltzmann constant (1.38 × 10 <sup>-23</sup> J K <sup>-1</sup> )	$N_s$	surface site density (mol m <sup>-2</sup> )
$k_c$	mass transfer coefficient (kg m <sup>-2</sup> s <sup>-1</sup> )	$O^*$	surface atomic oxygen
$f(\theta)$	sticking function	$P$	pressure (Pa)
$m$	mass (g)	$R$	universal gas constant (8.314 Pa m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )
$m_{molec}$	mass of one adsorbed molecule (g)	$R_p$	particle radius (m)
$n$	reaction order	$R_{O,th}$	theoretical oxygen transfer capacity (g g <sup>-1</sup> )
$r_i$	reaction rate (mol m <sup>-3</sup> s <sup>-1</sup> )	$S$	sticking probability
$t$	time (s)	$S_{BET}$	specific BET surface per unit mass (m g <sup>-2</sup> )
$u_z$	superficial gas velocity in the $z$ direction (m s <sup>-1</sup> )	$T$	temperature (K)
$r_{ij}$	reaction rate of reaction $j$ for species $i$ (mol m <sup>-3</sup> s <sup>-1</sup> )	$V_i$	species $i$ vacancy
$y_i$	mole fraction of species $i$ (mol mol <sup>-1</sup> )	$V$	volumetric flowrate (m <sup>3</sup> s <sup>-1</sup> )
$z$	height (m)	$X$	solid conversion
$C_i$	concentration of species $i$ (mol m <sup>-3</sup> )	$Z_w$	flux of incident molecules (molec m <sup>-1</sup> s <sup>-2</sup> )
$C_{i,b}$	concentration of species $i$ in the bulk phase (mol m <sup>-3</sup> )	<i>Greek letters</i>	
$C_{i,s}$	surface concentration of species $i$ (mol m <sup>-3</sup> )	$\epsilon$	bed porosity
$D_e$	effective diffusivity (m <sup>2</sup> s <sup>-1</sup> )	$\gamma_i$	normalized concentration of species $i$
$D_z$	axial dispersion coefficient (m <sup>2</sup> s <sup>-1</sup> )	$\rho_b$	bulk density (kg m <sup>-3</sup> )
$E_a$	activation energy (J mol <sup>-1</sup> )	$\rho_p$	particle density (kg m <sup>-3</sup> )
$Z_w$	flux of incident molecules (molec m <sup>-1</sup> s <sup>-2</sup> )	$\theta_i$	surface coverage of species $i$
$K_i$	equilibrium constant for reaction $i$		
$M_i$	molar mass of species $i$ (g mol <sup>-1</sup> )		
$N_{CO^*}$	adsorbed CO density (mol m <sup>-2</sup> )		

oxygen carrier, at least in its pure form, but the addition of iron and calcium oxides improve its mechanical resistance [23,24,22]. During calcination, pyrolusite, initially in the form of amorphous MnO<sub>2</sub>, decomposes into bixbyite (Mn<sub>2</sub>O<sub>3</sub>), hausmannite (Mn<sub>3</sub>O<sub>4</sub>), and manganosite (MnO). The prevalence of any specific phases depends on the oxygen partial pressure. Kononov et al. [25] measured Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> when heating pyrolusite under air at 1000 °C, but only MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> under argon. This last result is surprising when considering that pyrolusite (MnO<sub>2</sub>) decomposes at 535 °C into a mixture of bixbyite, hausmannite, manganosite and molecular oxygen [26].

Pyrolusite is an ideal oxygen carrier. Indeed, various patents involving pyrolusite were filed [27–29], 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<sub>3</sub>s and VOCs [30,31]. 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 [25]. Reducing the surface of a manganese oxide increases its basicity, and decreases its surface site density (less oxygen sites) [32]. In addition, the reduction creates new mineralogical phases (e.g. reduction from MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub>), which in turns swells the lattice, by further lowering the number of oxide sites (increased spacing) [32]. The increasing extent of reduction also decreases the Mn–O bond strength, due to the gradual replacement of Mn<sup>4+</sup> with the larger Mn<sup>3+</sup> cation [32]. The sole adsorption of CO also modifies the Mn–O bond energy [33]. 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 [30]. In addition, even in the absence of molecular gas-phase oxygen, pure unsupported manganese oxide reduces methane without coking [31], 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<sub>2</sub> into CO at high temperature due to the naturally occurring alkali promoters present with the manganese oxide phase. Imbihl and Demuth [34] postulated that CO<sub>2</sub> is activated into CO<sub>2</sub><sup>-</sup> over potassium promoters, then dissociates into CO and atomic surface oxygen, which rapidly integrates into the lattice. Busca [30] observed a strong IR peak at 2338 cm<sup>-1</sup> when heating Mn<sub>3</sub>O<sub>4</sub> in air at 400 °C, followed by vacuum. They associated this peak with trapped CO<sub>2</sub> (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<sub>2</sub> 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.

## 2. Material and methods

We sourced pyrolusite from Centra Africa (via Total SA France) and sieved it to recover the 90–106 μm diameter particles. Beside

**Table 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	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

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