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Kinetics model for the reduction of Fe_2O_3/Al_2O_3 by CO in Chemical Looping Combustion

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ABSTRACT

Kinetics model which describes intrinsic characteristics of reactions involved in Chemical Looping Combustion (CLC) can be used as a basic tool for reactor design and reactor modeling. To further develop previously studied sol-gel Fe_2O_3/Al_2O_3 oxygen carrier, this work performed a detailed kinetics investigation for the reduction from Fe_2O_3/Al_2O_3 to Fe_3O_4/Al_2O_3 by CO. In order to derive a reliable kinetics model, thermodynamics calculations were first performed to identify the reaction pathways with full CO_2 capture and no carbon deposition, excluding their influence. Experimental data at 673–773 K during thermogravimetric analyzer (TGA) tests was considered for kinetics analysis to attain good CLC performance. Finally, a widely used model-free method was employed to develop the kinetics model. Accordingly, a 3D nucleation and nuclei growth model with the model function $g(X) = [-\ln(1-X)]^{1/3}$, activation energy 270 kJ/mol and pre-exponential factor $1.6{\cdot}10^{12}s^{-1}$ was developed to describe the first half reduction from Fe_2O_3/Al_2O_3 to Fe_3O_4/Al_2O_3 by CO ($0 < X \leq 0.5$). Following this, the diffusion effects dominated the reduction process ($0.5 < X \leq 1$), which can be described by a 2D diffusion model function $g(X) = (1-X)\cdot\ln(1-X) + X$ with the activation energy and pre-exponential factor as 131 kJ/mol and $3.1{\cdot}10^3\ s^{-1}$, respectively. The whole kinetics model can be considered for the future application.

1. Introduction

The global energy requirement still depends highly on the transformation of fossil fuels, which results in the continuing increase of CO_2 emissions [1]. The impact of CO_2 level on the average temperature of Earth is crucial, since it is considered as the largest contributor to the greenhouse effect [2,3]. In order to mitigate CO_2 emission, clean combustion technologies for fossil fuels were developed in the past decades. Among them, Chemical Looping Combustion (CLC) has emerged as a most competitive technology due to its low cost for CO_2 capture [4]. The CLC concept based on the ideas of producing pure CO_2 [5] and improving thermal efficiency via intermediate reactions [6] was first introduced by Ishida et al. [7] to reduce exergy loss. Different to conventional combustion, CLC avoids the direct contact between combustion air and fuel (C_nH_{2m}) through the transportation of oxygen carrier (MeO_x), usually metal oxides, between air reactor (AR) and fuel reactor (FR). The oxygen carrier provides lattice oxygen for the combustion of fuel via reaction R1 in FR, where the oxygen carrier is converted to a reduced state (MeO_{x-1}). Then, MeO_{x-1} is circulated to the AR to regenerate via reaction R2, ready for new cycles. Theoretically, the gas stream at the outlet of FR contains only CO_2 and H_2O, where the separation of H_2O from CO_2 can be easily accomplished through a simple condensation process. In this way, high-energy penalty is prevented for the CO_2 separation in CLC with respect to the other CO_2 capture technologies.

$$C_nH_{2m} + (2n + m)MeO_x \rightarrow (2n + m)MeO_{x-1} + nCO_2(g) + mH_2O(g) \quad (R1)$$

$$MeO_{x-1} + 1/2O_2(g) \rightarrow MeO_x \quad (R2)$$

Oxygen carrier is a cornerstone for the CLC process, which has to efficiently accomplish the task of oxygen transference between AR and FR. Among the more than 700 oxygen carriers developed to date [8], Fe-based oxygen carriers have high potentials due to the characteristics of low cost, environmental friendliness, low agglomeration tendency and low attrition rate. In the published works, Fe-based oxygen carriers mainly include synthetic materials, minerals and industrial wastes. Regarding the latter two cases, extensive investigations were carried out [9–16], especially for ilmenite minerals which were recently considered for the scale-up to 50kW–1 MW pilot plants for CLC [12,13]. In comparison to the synthetic oxygen carriers, minerals and industrial

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Nomenclature

A	Pre-exponential factor, s^{-1}
C_nH_{2m}	Fuel
E	Activation energy, kJ/mol
$f(X)$	Differential form of reaction mechanism function
$g(X)$	Integral form of reaction mechanism function
m	Instantaneous mass of oxygen carrier, kg
MeO_x	Fully oxidized oxygen carrier
MeO_{x-1}	Fully reduced oxygen carrier
m_{ox}	Weight of completely oxidized oxygen carrier particles, kg
m_{red}	Weight of completely reduced oxygen carrier particles, kg
R	Universal gas constant, J/(mol K)
r^2	Linear coefficient
R_{OC}	Oxygen transport capacity
t	Reaction time, s
T	Temperature, K
X	Oxygen carrier conversion

Greek symbols

β	Heating rate for experimental tests, K/min
ω	Mass variation of oxygen carrier

Acronyms

AR	Air reactor
BET	Brunauer-Emmett-Teller
CLC	Chemical looping combustion
FR	Fuel reactor
ICSD	Inorganic crystal structure database
TGA	Thermogravimetric analyzer
TPR	Temperature programmed reduction
WGS	Water-Gas shift
XRD	X-ray diffraction

wastes possess the advantages of low cost. Nevertheless, minerals and industrial wastes always show lower reactivity than the synthetic ones in terms of coal combustion [17,18]. High reactivity of the synthetic oxygen carriers suggests a considerable decrease of materials inventory for CLC. In this context, a highly reactive Fe_2O_3/Al_2O_3 oxygen carrier was recently synthesized through sol-gel technique by Mei et al. [18]. During their tests in a fluidized bed reactor, the Fe_2O_3/Al_2O_3 oxygen carrier exhibited extremely high rates of char gasification and combustion over the other synthetic, mineral and industrial waste materials [18]. In this case, a very low solid inventory of around 600 kg/MW is adequate to reach a combustion efficiency of 99% at 1173 K.

For the further development of the sol-gel Fe_2O_3/Al_2O_3 oxygen carrier synthesized by Mei et al. [18], the reaction characteristics between the oxygen carrier and the gases involved in coal evolvement, i.e. CH_4, CO and H_2, must be thoroughly understood. Among them, the reaction kinetics is a basic tool for reactor design and modeling. Previous work determined the kinetics model for Fe_2O_3 reduction by H_2 based on a non-isothermal extrapolation method [19,20]. However, there is no work focused on the reaction kinetics of CO and the specific sol-gel Fe_2O_3/Al_2O_3 oxygen carrier. In fact, CO as a major component during the CLC of coals, its low reactivity with Fe_2O_3/Al_2O_3 dominates directly the concentration of CO_2 in the product gas stream, which finally affects the CO_2 capture. Although the Fe_2O_3/Al_2O_3 presents high reactivity with coal [18], the detailed reaction mechanism of CO and this oxygen carrier is not fully known. The knowledge of reaction kinetics of CO and Fe_2O_3/Al_2O_3 can assist the evaluation of reaction process, which can further be used to the optimization for full CO conversion to CO_2. More indeed, despite the Water-Gas Shift (WGS) reaction plays a role during the conversion of syngas-like (CO + H_2) fuels [21,22], the reactivity of this reaction may not be very relevant for kinetics model determination and oxygen carrier evaluation due to the low rate of WGS [23] and the origins of oxygen source from oxygen carrier instead of H_2O during CO combustion [21,22]. Therefore, the direct reaction of CO and oxygen carrier can be considered as a dominant pathway for CO combustion in syngas-like fuels. In this sense, it is highly necessary for the development of the kinetics model for the reduction of the sol-gel Fe_2O_3/Al_2O_3 and CO.

The objective of this work is to develop a kinetics model for the reduction of the sol-gel Fe_2O_3/Al_2O_3 oxygen carrier by CO. With this aim, thermodynamics calculations were first conducted to identify the dominant reactions for high CO_2 purity and no carbon formation, which is preferred in CLC. A series of experimental tests were carried out in a thermogravimetric analyzer (TGA) under various heating programs to understand the characteristics of Fe_2O_3/Al_2O_3 reduction by CO and to identify the main region for good CLC performance. Finally, based on the thermodynamic analysis, TGA tests and kinetics analysis, kinetics model was developed for the specific sol-gel Fe_2O_3/Al_2O_3 oxygen carrier during its reduction to Fe_3O_4/Al_2O_3 by CO.

2. Experimental

2.1. Oxygen carrier

The oxygen carrier particles are the same as that used in our previous work, which was concluded as a highly reactive material for CLC of coal [18]. This oxygen carrier containing 60 wt.% Fe_2O_3 and 40 wt.% Al_2O_3 was prepared through a sol-gel technique and calcined at 1473 K for 12 h in air. Detailed procedures of the oxygen carrier preparation can be found in our previous work [18]. Main properties of the fresh oxygen carrier are given in Table 1. The oxygen carrier particles were sieved to diameters of 0.125–0.180 mm, a desirable size for the fluidization in circulation fluidized beds. Crushing strength of the particles is the average strength for the fracture of 20 randomly-selected particles, measured by a Shimpo FGJ-5 apparatus, which is 1.39N and high enough for the use in fluidized beds [24]. The X-ray diffraction (XRD) patterns of the fresh and reduced materials were acquired in a Shimadzu 7000 diffractometer using a Ni-filtered Cu Kα radiation, which is presented in Fig. 1. The phase composition of the oxygen carrier was identified using the inorganic crystal structure database (ICSD). As shown in Fig. 1, the fresh oxygen carrier particles mainly contain Fe_2O_3 and Al_2O_3 phases. Real density of the material was determined in a Micromeritics AccuPyc 1330 picnometer, taking a value of 4653 kg/m^3. Specific surface area of the oxygen carrier particles is 1.39 m^2/g given by a Micromeritics ASAP2020 instrument according to the Brunauer–-Emmett–Teller (BET) method. Finally, the oxygen transport capacity R_{OC} of the oxygen carrier was calculated as 0.02, considering the transformation from Fe_2O_3/Al_2O_3 to Fe_3O_4/Al_2O_3 during the reduction in this work.

Table 1
Main properties of the fresh Fe_2O_3/Al_2O_3 oxygen carrier.

Mass fraction of Fe_2O_3 (wt.%)	60
Particle size (mm)	0.125–0.180
Real density (kg/m^3)	4653
Crushing strength (N)	1.39
BET surface area (m^2/g)	1.39
Oxygen transport capacity, R_{OC}	0.02