Chemical looping reforming of methane using magnetite as oxygen carrier: Structure evolution and reduction kinetics

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HIGHLIGHTS

- The magnetite concentrates are evidenced to be feasibility for CLRM.
- The magnetite OCs can produce H_2 and syngas with high stable performance.
- The initial reduction is controlled by the phase boundary-controlled mechanism.

GRAPHICAL ABSTRACT

In the present work, we describe for the first time the reactivity of magnetite oxygen carriers for coproduction of syngas and hydrogen via chemical looping reforming of methane. When the magnetite reaches its stable state after successive redox cycling, the reduction kinetics for the recycled oxygen carriers was performed by using a TGA method. From the kinetics study, the reduction mechanism and activation energy are presented.
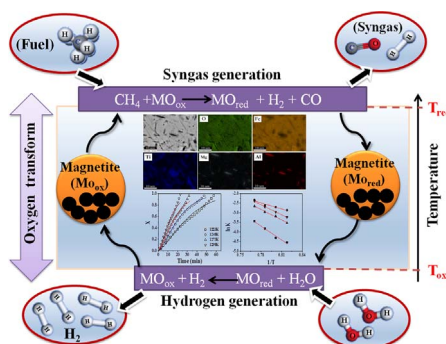
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ABSTRACT

One of the most important issues for chemical looping technology is to find low-cost oxygen carriers. This work presents the investigation on using a Panzhihua (China) magnetite as oxygen carrier for chemical looping reforming of methane (CLRM). The reactivity for coproduction of syngas and hydrogen was tested by an isothermal redox experiment using methane as a reducing fuel and steam as an oxidizing gas. The kinetics study was performed on both the fresh and recycled magnetite oxygen carriers. In the redox experiments, the produced hydrogen and syngas in a H_2/CO molar ratio of 2.0 can be stably obtained with high selectivity (ca. 95.1% for syngas and ca. 96.2% for H_2). The yields of hydrogen from the original and calcinated magnetite after successive cycling are 4.94 and 5.25 mmol/g, respectively. From the kinetic study via a thermogravimetric analyzer (TGA) method, it is found that the reduction of original magnetite to wüstite is well represented by the phase boundary-controlled (contracting cylinder) mechanism, and the 1-D nuclei nucleation and growth integrated with diffusion mechanism can be successfully applied to describe the reduction of calcined magnetite. The activation energy for the reduction of original magnetite is 93.02 kJ/mol, which slightly decreases to 86.90 kJ/mol after successive

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cycling due to the formation of pores inside the oxygen carriers. This work gives full evidence to the feasibility of using magnetite concentrates as low-cost oxygen carrier for the CLRM system.

Nomenclature

		m	constant that varies with the geometry of the system
		r	least square coefficient
E_a	activation energy, kJ/mol	t	reaction time, min
$f(x)$	solid-state reaction rate equations which is a function of the reaction mechanism	T	absolute temperature, K
		w	weight of the measured sample, mg
$g(x)$	reaction mechanism integral form	x	fractional conversion of metal oxides
k	reaction rate constant, 10^{-4}/min		

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1. Introduction

Hydrogen is regarded as the most promising secondary energy in the 21st century, and syngas (a mixture of CO and H_2) is an important chemical resource for liquid fuel synthesis (e.g. Fischer–Tropsch or methanol synthesis) [1–5]. Chemical looping reforming of methane (CLRM) is a novel technology for co-production of syngas and pure hydrogen [6–13]. This process involves the use of solid oxygen-containing materials as oxygen carriers (OCs) to implement a two-step reduction-oxidation (redox) cycle. Methane firstly reacts with the oxygen carrier to produce syngas with a H_2/CO ratio of 2.0, and then the reduced oxygen carrier can be oxidized by steam to restore its initial state for hydrogen generation. Compared with the traditional methane steam reforming technology, the produced hydrogen from the CLRM process is never mixed with the CH_4 or CO, and pure H_2 can therefore be readily obtained after condensation of excess steam and removal of the liquid water. This eliminates the need of an additional energy supply for H_2 separation. In addition, the produced syngas with a H_2/CO ratio of 2.0 in the first step is suitable for further methanol production or Fischer–Tropsch synthesis [1].

The design and elaboration of suitable oxygen carriers with high activity is one of the key issues to perform the CLRM process. In general, the oxygen carriers must possess high reactivity, superior oxygen transport capacity, high selectivity and excellent redox property [14–19]. Metal oxides, such as Fe_3O_4/Fe_2O_3, NiO, CuO, MnO_2, CeO_2, Co_3O_4, and perovskite-type oxides as well as their blends have been intensively tested as oxygen carriers in either gaseous or solid fuels [14,18,20–33]. To achieve hydrogen production in the second step of CLRM, the reduced OC should be able to be regenerated by water. From the thermodynamic point of view, copper, manganese and they oxides cannot be oxidized by water to higher valence. Since CeO_2 and Co_3O_4 are expensive, they are not suitable as a substrate for large scale production of oxygen carriers. Diego et al. [29] proposed to use NiO/γ-Al_2O_3 as oxygen carrier for chemical looping reforming of methane, and they found that, in the temperature range of 800–900 °C, CH_4 conversion was as high as 98%. However, the use of Ni-based OCs should be very careful because of its toxicity. High activity and selectivity for CLRM were also observed over perovskite-type $LaFeO_3$-based oxygen carrier [15,32], but the complex preparation period is a challenge for its application.

Iron-based oxides are considered as a promising candidate due to the easy handling, relatively low cost, nontoxicity, and environmentally friendly features [20,26–28]. Steinfeld et al. [20] firstly thermodynamically examined the reaction of Fe_3O_4 with CH_4. At 1 atm and temperatures above 1300 K, the chemical equilibrium components consist of metallic iron in the solid phase and a mixture of 66.7% H_2 and 33.3% CO in the gaseous phase. They proposed that this process could offer simultaneous production of iron from its ores and of syngas from natural gas, without discharging CO_2 and other pollutants to the environment. The CLRM over iron oxides for hydrogen production were also investigated by Kang et al. [26], and CO-free hydrogen (H_2) and

syngas with a H_2/(2CO + 3CO_2) molar ratio of 0.65 were obtained. It is well accepted that complex metal oxides usually have better properties than single ones. The main objectives desired from this viewpoint aim to increase the reactivity and stability of OC, improve the mechanical strength of particles, minimize carbon deposition and avoid using toxic and expensive ingredients. Kang et al. [27] deduced that the addition of Cu to $CuFe_2O_4$ could enhance reduction kinetics, decrease reduction temperature and prevent carbide and graphite formation. He et al. [28] prepared a series of CeO_2-based oxygen carriers by adding Fe, Cu, and Mn oxides for CLRM. As for the Ce-Fe-O oxygen carrier, methane was converted to syngas with a H_2/CO molar ratio close to 2:1.

Another important issue for the development of chemical looping technology is to find low-cost and environmental friendly oxygen carriers. Industrial residues, ores and minerals or by-products are good choices for this purpose. Mendiara et al. [34] conducted a study on the reactivity of an iron waste material from aluminum manufacture with different gases by means of a batch fluidized bed reactor. The experiments showed that it needs high-temperature and long time for obtaining high CH_4 conversion. Song et al. [35] investigated the chemical looping conversion of methane using calcium sulfate as oxygen carrier. The results showed that this oxygen carrier own high reduction reactivity and stability in a long-term redox test. Ilmenite, a natural iron-containing mineral, was also studied as a possible oxygen carrier for chemical looping process [36–41]. The results indicated that some impurity components in this mineral are favorable for the reaction, which revealed high ability to resist sintering and agglomerate at high temperatures. Leion et al. [37] tested the cyclic stability of ilmenite for chemical looping combustion of syngas and found that the oxygen carrier keep stable after 37 cycles or 3 days of experiments. An experimental campaign was also conducted by Pröll et al. [38] at a fluidized bed installation for chemical looping of gaseous fuels using natural ilmenite as oxygen carrier. It was found that the natural olivine as an additive could improve the methane conversion. Cuadrat et al. [39] showed that the reactivity of ilmenite for methane oxidation increased with the number of cycles. The reaction rate was maximum and constant at the beginning of the reducing period until an ilmenite mass conversion of about 0.99, and this value did not decrease for 100 cycles. Wang et al. [42] reported that copper ore performed good redox ability, resistance to agglomeration/sintering, and high reactivity in a chemical looping process. However, the gasification efficiency was relatively low. Schmitz et al. [43] showed that manganese ores as oxygen carrier have a good performance and reached more than 90% gas conversion at relevant conditions. Particle lifetime based on fine productions was in the range of 99–284 h.

It should be stressed that CLRM is totally different with the CLC technology. When using iron-based oxygen carrier for a CLRM process, the reduced iron oxides cannot be completely reoxidized by water to Fe_2O_3 (only to Fe_3O_4) in the second step [10,31]. For an oxygen carrier mainly containing Fe_2O_3, the transformation of Fe_2O_3 to Fe_3O_4 after redox cycling would result in huge dimensional changes. This is very detrimental to the structural stability of oxygen carrier, especially for a