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Article

Synthesis of three-dimensionally ordered macroporous LaFeO_3 perovskites and their performance for chemical-looping reforming of methane

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ABSTRACT

Three-dimensionally ordered macroporous (3DOM) LaFeO_3 perovskite-type oxides were synthesized using a polystyrene colloidal crystal templating method. The obtained 3DOM LaFeO_3 was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The reactivity of the perovskite-type oxides was evaluated using temperature-programmed reduction and multicyclic redox reactions by exposing them to an alternating methane and air atmosphere. The methane oxidation performance of the oxides was investigated in a fixed-bed reactor. The effect of the self-assembly method on the structure of the polystyrene template was also studied. A vertical deposition method yielded a more uniform and orderly polystyrene template than those obtained by centrifugation and evaporation techniques. The solvent and concentration of the precursor solution were the major factors to affect the prepared 3DOM perovskite. SEM analysis showed that samples synthesized with ethanol precursor solvent exhibited a better 3DOM structure than those produced with ethylene glycol, and that 1.0 mol/L may be an optimal precursor solution concentration. XRD and FTIR results suggested that the obtained 3DOM LaFeO_3 was pure crystalline perovskite. Two kinds of oxygen species were found to exist on the 3DOM perovskites: surface adsorbed oxygen and bulk lattice oxygen. The surface oxygen contributed to the complete oxidization of methane to CO_2 and H_2O because of its higher reactivity, while the bulk lattice oxygen tended towards partial methane oxidation to H_2 and CO. The available oxygen in the 3DOM LaFeO_3 was higher than that of the same mass of non-3DOM LaFeO_3 during the partial oxidation of methane. Methane was partially oxidized into syngas with a H_2/CO ratio of around 2:1 in a wide time range of the reactions. The generated $\text{H}_2/\text{CO} = 2$ syngas was suitable for subsequent gas-to-liquids processes, such as Fischer-Tropsch and/or methanol synthesis.

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1. Introduction

Chemical-looping combustion (CLC) involves the use of a

metal oxide as an oxygen carrier to transfer oxygen from the combustion air to the fuel, hence avoiding direct contact between air and fuel. CO_2 and H_2O are thus inherently separated

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from the other non-condensable components of the flue gas, such as N_2 and unused O_2 [1,2]. Chemical-looping reforming (CLR) uses the same basic principles as CLC with the main difference that the target products in CLR are synthesis gas (H_2 and CO) instead of heat [3]. For the CLR of methane, a suitable oxygen carrier is circulated between two reactors as in CLC. Methane is partially oxidized to synthesis gas by the lattice oxygen of the oxygen carrier in the first reactor (the fuel reactor), and the reduced oxygen carrier is re-oxidized by air in the second reactor (the air reactor). In this way the produced synthesis gas is not diluted with N_2 [4]. The success of the CLR process is highly dependent on finding suitable oxygen carriers that have sufficiently high conversion rates during redox reactions, high comminution and agglomeration resistance, and are economical and environmentally friendly. The transition metal oxides Ni, Cu, Fe, Co, and Mn have been studied as oxygen carriers for CLR [5–7]. Various support materials such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , $NiAl_2O_4$, and $MgAl_2O_4$ are usually used as an inert binder to enhance the reactivity, durability, and fluidizability of the oxygen carrier particles. While nickel catalysts have been reported as having good performance for the dry reforming of methane to generate synthesis gas [8,9], these oxygen carriers still face technical barriers to commercialization, such as carbon deposition and agglomeration.

Perovskite-type complex metal oxides are a series of mixed oxides with general formula ABO_3 , where A is usually a lanthanide ion and/or alkaline earth metal and B is a transition metal ion. The oxidation activity of perovskite-type oxides can be comparable to that of noble metal catalysts under suitable conditions [10]. In view of their high thermal stability, good mechanical properties, as well as decent activity, perovskite-type oxides are candidates for the manufacture of various high temperature electrochemical devices, as redox reaction catalysts and as oxygen carriers for CLC processes [11]. Common perovskite-type catalysts, however, often have small specific surface area because they are prepared after high temperature calcinations.

Three-dimensionally ordered macroporous (3DOM) materials with uniform pore size in the sub-micrometer range (> 50 nm) have attracted much attention in the last decade because of their potential applications in catalysts, catalyst supports, photonic crystals, and separation. The macropores of these materials are interconnected through windows that form as a result of contact between the template spheres prior to infiltration of the precursor solution. Thus, 3DOM materials have a high porosity, as much as ca. 74% theoretically [12]. When 3DOM materials are used as oxygen carriers in CLR, the macroporous network allows the reactant to enter the inner pores of the particles. These pores allow easy mass transfer of reducing gases through the macroporous structure to active sites with less diffusional resistance, and increase the available active surface remarkably. In addition, the macropores of 3DOM materials are large enough to permit carbon particles to enter the inner pores where the carbon combustion reaction can occur. Zheng et al. [13,14] prepared 3DOM $LaFeO_3$ and $LaMn_{1-x}Fe_xO_3$ perovskites and investigated their catalytic performance for diesel soot combustion. They observed that

3DOM perovskites have higher activity than nano-perovskites for soot combustion, and that the activity of the 3DOM perovskites increased with pore diameter.

In the present work, 3DOM $LaFeO_3$ perovskite-type oxides were prepared by a polystyrene (PS) colloidal crystal templating method. The obtained 3DOM $LaFeO_3$ was studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). In addition, the reactivity of the materials was evaluated by temperature-programmed reduction (TPR), and its redox behavior was investigated by exposure to an alternating methane and air atmosphere. The methane oxidation performance of the perovskite-type oxide was investigated in a fixed-bed reactor.

2. Experimental

2.1. Synthesis of 3DOM $LaFeO_3$

All chemicals used were of reagent grade. PS spheres are typically synthesized by emulsion polymerization, soap free emulsion polymerization, or seed emulsion polymerization. The soap free emulsion polymerization method was used to prepare PS spheres in this work because it yielded PS spheres with good monodispersity. Washed and distilled styrene was slowly added to a four necked round-bottomed flask equipped with a magnetic stirrer and filled with deionized water (800 ml) heated to $70\text{ }^\circ\text{C}$ using a hot water bath. A thermometer and a water-cooling condenser were attached to the flask, and pure N_2 was fed into the flask through a pipet vessel to remove air. Then, 0.663 g of potassium persulfate (KPS) was dissolved in beaker containing 100 ml deionized water heated to $70\text{ }^\circ\text{C}$, after which the resulting solution was added to the styrene and water solution. The mixture was subsequently polymerized for 24 h under constant stirring (400 r/min) and N_2 bubbling. The resulting microsphere emulsion was allowed to cool to room temperature and was then filtered to remove large agglomerates. The colloidal PS crystal microsphere emulsion was self-assembled by either centrifugation, evaporation, or vertical deposition to obtain highly ordered PS microsphere arrays.

Lanthanum nitrate hydrate ($La(NO_3)_3 \cdot 6H_2O$) and iron nitrate hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in alcoholic solution at a 1:1 molar ratio, and an equimolar (metal ion) amount of citric acid was added as a complexing agent. The colloidal PS crystals were soaked in the solution for 3 h. Excess solution was removed from the impregnated colloidal PS crystals by vacuum filtration. The obtained sample was allowed to dry in air overnight at room temperature and was then calcined in a muffle oven at a rate of $1\text{ }^\circ\text{C}/\text{min}$ from room temperature to $500\text{ }^\circ\text{C}$ and held for 3 h. The temperature was then increased at a rate of $1\text{ }^\circ\text{C}/\text{min}$ to $750\text{ }^\circ\text{C}$ and held for 4 h. To compare the properties of 3DOM $LaFeO_3$ with those of nonporous $LaFeO_3$, ultra-fine $LaFeO_3$ powder without 3DOM structure was prepared by a sol-gel method.

2.2. Characterization

The crystal phases of the oxides were analyzed by XRD us-

ing a Japan Science D/max-R diffractometer with Cu $K\alpha$ radiation at an operating voltage of 40 kV and current of 40 mA and the diffraction angle (2θ) was scanned from 10° to 90° . The morphology of the perovskite-type oxides was studied by SEM on a Hitachi S4800 instrument. FTIR spectra were recorded on a Bruker TENSOR27 instrument equipped with a quartz sample holder with KBr windows.

2.3. Reactivity tests

The reactivity of the 3DOM LaFeO₃ perovskite-type oxides was evaluated using TPR on a Quantachrome Instruments PULSAR TPR/TPD. The TPR experiments were conducted in 5.0 vol% H₂ balanced with helium at a flow rate of 20 cm³/min from room temperature to 850 °C with a heating rate of 10 °C/min. The composition of the outlet gas was monitored using a quadrupole mass spectrometer.

Reduction-oxidation (redox) multicycles were conducted in a thermogravimetric analyzer (TGA), as reported in detail elsewhere [15]. Briefly, the reactor, which consisted of concentric double quartz tubes, was placed into a tubular furnace. The inner and outer quartz tubes were 30 mm and 40 mm in diameter, respectively. For each test, 1.0 g of oxygen carrier was placed on a 28 mm diameter quartz pan suspended from the electric microbalance by a thin stainless steel wire. The reactant gas was introduced into the reactor from the top of the outer tube to ensure that the reactant gas was preheated to the specified temperature. Prior to reactivity tests, the oxygen carrier was heated to 600 °C at a rate of 10 °C/min in flowing air and held for 1 h, after which N₂ was introduced to the reactor for 30 min to remove all air from the reactor. When the temperature reached the desired value, CH₄ and air were alternately introduced into the reaction tube. The temperature of the furnace was maintained using an electronic controller, and the weight of the oxygen carrier particles was continuously recorded by a computer connected to the microbalance. To avoid mixing of the air and methane during the shift between the reduction and oxidation periods, N₂ gas was introduced for 600 s after each period.

The methane oxidation activity of the oxides (1 g in each test) was evaluated in a fixed-bed quartz reactor (10 mm i.d.) under atmospheric pressure at 850 °C. A mixture of 40.0 vol% methane with nitrogen as balance was used as the feed gas, and its flow rate was set at 20 ml/min. The product gases from the reactor were collected with gas bags and analyzed by gas chromatography (Shimadzu GC-20B-1 gas chromatograph).

3. Results and discussion

3.1. Effect of the self-assembly method on the structure of the PS template

Styrene addition and polymerization time are the crucial factors affecting the size of PS spheres during their preparation. In our previous work, we discussed the effect of these two factors on PS sphere diameter in detail [16]. In the present work, we focused on exploring the effect of self-assembly methods on

the structure of the resulting PS template. Centrifugation, gravity deposition, vertical deposition, and evaporation are typically used to prepare highly ordered colloidal crystalline templates. Polymer templates, which support the precursor while it converts into a solid state skeleton at low calcining temperature, play an important role in the successful synthesis of 3DOM materials. Because of the disadvantages of the gravity deposition method, including harsh conditions and long preparation period, only centrifugation, evaporation, and vertical deposition were used to assemble the PS templates in the present work. The details of the procedures for these self-assembly methods have been described in the literature [16]. The PS templates assembled by the different methods are shown in Fig. 1.

As shown in Fig. 1, the colloidal crystal template produced by evaporation did not exhibit an orderly arranged structure, indicating that it was difficult to assemble the PS microspheres into three-dimensionally ordered arrays through evaporation alone. The observed disorderly template can be attributed to the fast and uncontrollable volatilization of the solvent preventing uniform accumulation and formation of an ordered lattice. In comparison, more orderly assembled crystalline arrays were formed by the centrifugation method (see Fig. 1(b-1) and (b-2)). The colloidal crystal template had a good three-dimensionally ordered arrangement with well-ordered and uniform polycrystalline structure. The centrifugation method possesses the advantage of a short preparation cycle, giving rapidly settling and compact templates. To obtain a high quality colloidal crystal template, the centrifuge speed must be strictly controlled because the microspheres will be deformed at an excessive centrifuge speed. It has been reported in the

Fig. 1. SEM images of the colloidal crystal polystyrene template prepared by different methods. (a) Evaporation; (b) Centrifugation; (c) Vertical deposition.

literature [10] that templates are more uniform when formed below a rotational speed of 2800 r/min.

The microstructure of the colloidal crystal template prepared by vertical deposition is shown in Fig. 1(c-1) and (c-2). It is clear that the template assembled using this method was highly ordered with less defects and agglomeration in comparison with those produced by evaporation and centrifugation. As seen in Fig. 1(c-1), a florid light could be observed while changing the viewing angle, namely Bragg diffraction, which is the typical diffraction behavior of an orderly array. This indicates that the template was in a good three-dimensionally ordered arrangement. Among the three microsphere self-assembly methods, vertical deposition clearly yielded the most uniform and orderly arrays. However, vertical deposition also has disadvantages such as long operation time and low product yield. Therefore, because of its advantages of short assembly time and well assembled templates, the authors' laboratory presently uses centrifugation self-assembly for the preparation of 3DOM materials.

3.2. Effect of precursor solution

3.2.1. Solvent effect

To synthesize 3DOM perovskite-type metal oxides by the present colloidal crystal templating method, the three-dimensionally ordered colloidal crystal templates were impregnated with the precursor solution and then dried in air overnight. Finally, the dried precursor/template mixtures were calcined in air to remove the polymer templates. The solvent and the precursor solution concentration were the important factors affecting the resulting 3DOM materials. Figure 2 shows the SEM images of the LaFeO_3 perovskite-type oxides produced by impregnation of the templates in precursor solutions with ethanol and ethylene glycol as solvents.

The SEM images indicate that the sample prepared using ethanol as precursor solvent exhibited a good 3DOM structure containing an interconnected macroporous framework. The next layer of the macroporous structure is clearly visible in the enlarged SEM image and the voids are interconnected through open windows, which formed because no precursor solution was present in the contacting areas between the polymer spheres. However, the materials obtained with ethylene glycol as the precursor solvent exhibited apparent agglomeration and no obvious ordered macroporous structure. It is supposed that this was caused by the fact that ethylene glycol solution has a higher viscosity, resulting in the solution being unable to wet and penetrate the PS templates very well. Therefore, thin and

Fig. 2. SEM images of LaFeO_3 perovskite-type oxides produced with different precursor solvents. (a) Ethanol; (b) Ethylene glycol.

defective walls were produced in the interspace between the microspheres because the precursor solution could not fill the entire void in the PS template. The solid walls did not have enough strength to support themselves and tended to collapse easily during calcination. Sadakane and co-workers [17] found that addition of 40 vol% methanol to ethylene glycol solvent inhibited the collapse of macroporous structure during calcination. Therefore, ethanol or ethylene glycol mixed with a certain percentage of methanol is expected to be good solvent for preparing 3DOM perovskite-type oxides using the PS colloidal crystal templating method.

3.2.2. Effect of precursor solution concentration

Besides the type of solvent, the concentration of the precursor solution is another important factor that affects the formation of a 3DOM skeleton. A low precursor solution concentration is beneficial to allow the precursor to penetrate into the voids in the PS template. However, if the concentration of the precursor solution is too low, repeated filling may be necessary to form an interconnected network. Otherwise, the reduced filling content of the precursor may result in thinner solid walls which cannot self-support and easily collapse during calcination. Conversely, if the concentration of the precursor solution is too high, it is difficult for the precursor to occupy all the interstitial space inside the template because of its higher viscosity, and the ordering and regularity of the macroporous structure is weakened. Figure 3 shows SEM images of LaFeO_3 perovskites prepared using ethanol solutions with precursor concentrations of 0.3, 0.5, 0.8, and 1.0 mol/L. It was observed that the 3DOM structure of the material produced with a precursor concentration of 0.3 mol/L was almost totally collapsed, and only a few pores could be found on the surface. For precursor concentrations of 0.5 and 0.8 mol/L, the 3DOM structure was formed, but some of the interconnected walls were collapsed. A well-ordered 3DOM structure was obtained for the sample prepared with a precursor concentration of 1.0 mol/L. As shown in Fig. 3(d), the sample consisted of a skeleton surrounding uniform close-packed macropores interconnected

Fig. 3. SEM images of LaFeO_3 perovskite-type oxides prepared with ethanol solutions of different precursor concentrations. (a) 0.3 mol/L; (b) 0.5 mol/L; (c) 0.8 mol/L; (d) 1.0 mol/L.

Fig. 4. XRD patterns of as-prepared and reacted LaFeO_3 perovskite oxygen carriers.

through small windows. Therefore, 1.0 mol/L may be the optimum precursor concentration to prepare 3DOM LaFeO_3 perovskites. Higher precursor solution concentrations are usually diluted in alcohol or methanol before infiltration of the template spheres [18]. It is worth noting that part of the 3DOM structure of the material may be collapsed in the course of any redox reactions.

3.3. Characterization of the oxygen carrier

3.3.1. XRD

As-prepared and used 3DOM LaFeO_3 perovskites were examined by XRD to identify the crystalline phases formed (Fig. 4). The used sample was that regenerated after multicyclic redox reactions. The XRD patterns of the as-synthesized oxides were in good agreement with JCPDS card 75-0541, meaning that the sample consisted of monophasic crystalline perovskite with orthorhombic structure. Previous studies have reported the detection of La_2O_3 and carbon deposition on the surface of perovskites in a reduced state [15]. As shown in Fig. 4, however, the regenerated oxides recovered to a pure perovskite crystalline phase after successive cyclic redox reactions, which means that the present 3DOM perovskites have good repeatability.

3.3.2. FTIR spectroscopy

The measurement of vibrational frequencies by FTIR is a fundamental technique in the determination of the crystalline structure of a material [19]. The FTIR spectrum of the prepared 3DOM LaFeO_3 perovskite-type oxide is presented in Fig. 5. The oxide produced a strong and intense band at around 560 cm^{-1} , which is the most important absorption band of the perovskite structure and is attributed to the stretching vibration and/or asymmetrical lengthening of the Fe–O bond [20]. The widening of this band and/or the appearance of a shoulder indicate a structure with lower symmetry. The bands at 1458 and 1637 cm^{-1} were assigned to the asymmetric and symmetric O–C–O stretching vibration of the carboxylate group [21]. The O–C–O bond in the as-prepared samples may have existed in the form of segregated carbonate phases formed between metal ions and the carbon in the polymer template during calcination. A broad band appeared at 3400 cm^{-1} due to the characteristic length-

Fig. 5. FTIR spectrum of the 3DOM LaFeO_3 perovskite-type oxide.

ening of the O–H bond of water, the presence of which was caused by exposure of the perovskite to environmental humidity.

3.3.3. Specific surface area

It is well known that the higher surface area of perovskite is beneficial to its performance in catalytic and other applications. The surface area of the 3DOM LaFeO_3 perovskite prepared in this work was measured by mercury intrusion porosimetry (MIP), while those of the nano- LaFeO_3 perovskites were detected using the Brunauer-Emmett-Teller (BET) method. It was found that the 3DOM perovskite had a surface area of $44.023\text{ m}^2/\text{g}$, apparently higher than that of the nano- LaFeO_3 powder ($11.636\text{ m}^2/\text{g}$). Thus, the better reactivity of 3DOM LaFeO_3 compared with that of nano- LaFeO_3 can be partially explained by its higher surface area.

3.4. Reactivity tests

3.4.1. TPR

TPR was performed to study the reducibility of the prepared 3DOM LaFeO_3 perovskite-type oxide. It has been reported that oxygen vacancies can be formed in a perovskite-type oxide when it is heated in inert atmosphere at high temperature [22]. These vacancies are filled with adsorbed oxygen while charge compensation is provided by partial oxidation of the metal B ion. For LaFeO_3 perovskite-type oxides, part of the Fe^{3+} ions is oxidized to Fe^{4+} during calcination. Two types of perovskite oxygen species, α and β , participate in the oxidation reaction of hydrogen. Typically, α oxygen is non-stoichiometric oxygen, including excess oxygen and oxygen adsorbed on oxygen deficiency sites, while β oxygen is associated with the lattice oxygen of B-site cations with high oxidative state or with oxygen species occupying inner vacancies. The H_2 -TPR profile of the present 3DOM LaFeO_3 perovskite-type oxide is shown in Fig. 6 alongside that of non-3DOM LaFeO_3 for comparison.

It can be seen that the TPR profile of the 3DOM LaFeO_3 perovskite exhibited two distinct reduction peaks. The first reduction peak, the α peak, took place at $400\text{ }^\circ\text{C}$ and reached a maximum at $580\text{ }^\circ\text{C}$ with a shoulder at $500\text{ }^\circ\text{C}$. This peak is attributed to the reduction of α -oxygen and a fraction of Fe^{4+} formed by cation deficiency. The second reduction peak, the β

Fig. 6. TPR profiles of LaFeO₃ perovskites.

peak, was narrow and sharp with an onset temperature of 650 °C, reaching a defined maximum at 700 °C. This reduction zone is associated with the reduction of B-site ions to lower valences, in this case, reducing Fe⁴⁺ and Fe³⁺ to Fe²⁺ or metallic iron. The presence of the β peak and its onset temperature can be adopted as a qualitative description of catalyst reducibility and oxygen mobility within the oxide. Both of these parameters are fundamental to describe the catalytic activity and reactivity of the oxides. The TPR profile of the non-3DOM LaFeO₃ displayed two broad peaks spanning the temperature ranges 450–650 °C and 650–800 °C. However, these two peaks overlap each other, suggesting that the α and β oxygen species in the non-3DOM LaFeO₃ had similar activity.

In comparison, a slight shift towards lower temperature was observed for the reduction peaks of the 3DOM LaFeO₃ TPR profile. This shift on can be plausibly explained by the remarkable increase in specific surface area and oxygen vacancy concentration as well as the decrease in oxide particle size of the present 3DOM oxides. As mentioned above, the lower onset temperatures of the reduction peaks suggest that the oxide had better reactivity and oxygen mobility. Therefore, the present 3DOM LaFeO₃ exhibited better activity than the non-3DOM LaFeO₃ nano-powder.

3.4.2. Redox multicyclic reactivity

To test the redox multicyclic reactivity of the 3DOM LaFeO₃ perovskite-type oxide, redox multicycles of an oxide sample exposed to alternating methane and air conditions were carried out in the TGA reactor at 850 °C. Here, we used the degree of oxidation to measure oxygen carrier conversion during the redox cycles. The degree of oxidation was defined as:

$$X = (m - m_{\text{red}}) / (m_{\text{ox}} - m_{\text{red}}) \quad (1)$$

where m is the instantaneous mass of the sample, m_{ox} is the mass of the sample when fully oxidized, and m_{red} is the mass of the sample in the reduced form. The reduced form is either the metal or a metal oxide with lower oxygen content. Therefore, the difference between m_{ox} and m_{red} in Eq. (1) is the maximum amount of active oxygen, which can be removed through reaction with methane in the oxygen carrier. m is equal to m_{ox} when the sample is fully oxidized, and m is equal to m_{red} when it is fully reduced. Hence, $X = 1$ for complete oxidation, and $X = 0$ for complete reduction. In this work, the difference between m_{ox}

and m_{red} is calculated on the basis of the following transformation: LaFeO₃–LaFeO_{3-δ} ($\delta = 2$). This means that LaFeO is assumed to be the completely reduced form of the oxide in this work. In other words, when LaFeO₃ is reduced to LaFeO, X is equal to zero.

The perovskites were tested for twenty redox cycles at 850 °C. Stable reactivity was observed for both types of oxygen carrier during the twenty cycle test. The degree of oxidation of 3DOM LaFeO₃ and non-3DOM LaFeO₃ as a function of time for the first five redox cycles at 850 °C is shown in Fig. 7. For the 3DOM LaFeO₃ oxygen carrier, the reaction rate was fast when the degree of oxidation changed from 1.0 to 0.4 during the reduction stage. This indicates that 60% of the active oxygen was used as oxidant when the oxygen carrier was exposed to methane atmosphere. If the oxygen carrier was allowed to further reduce below an oxidation degree of 0.4, the reaction rate became very slow. Therefore, when the degree of oxidation became close to 0.4, we switched the reacting atmosphere from methane to air to regenerate the oxygen carrier. The oxidation rate of the reduced oxygen carriers in flowing air was considerably faster than their reduction rate. This suggests that the 3DOM LaFeO₃ oxide had good regenerability. In comparison with the 3DOM LaFeO₃, non-3DOM LaFeO₃ gave a small degree of oxidation change, from 1.0 to 0.65, during the reduction stage, which means that only 35% of the active oxygen reacted with methane. It is therefore clear that the present 3DOM LaFeO₃ provided a greater source of oxygen than the same mass of non-3DOM LaFeO₃ powder during methane oxidation. This was probably attributable to the macroporous network in the 3DOM LaFeO₃ allowing easy penetration of oxygen through the bulk and less diffusional resistance from the inner of the particles to the active sites at the surface. The 3D macropores and the high porosity permit more facile transport of gaseous reactants and ions compared with nano-particle aggregates. Therefore, the availability of oxygen in the 3DOM LaFeO₃ was higher than that of the non-3DOM LaFeO₃ particles.

As shown in Fig. 7, non-3DOM LaFeO₃ took approximately 12700 s to finish 5 redox cycles, which is shorter than that needed with the 3DOM LaFeO₃, 15900 s. It is worth noting that about 60% of the active oxygen in the 3DOM LaFeO₃ reacted with methane during the redox cycles, whereas only 35% of the

Fig. 7. Degree of oxidation, X , as a function of time for the first five redox cycles of 3DOM LaFeO₃ and non-3DOM LaFeO₃.

Fig. 8. Fractions of gas products and H_2/CO molar ratio as a function of time during methane oxidation by 3DOM $LaFeO_3$.

non-3DOM $LaFeO_3$ active oxygen reacted with methane. If the release of oxygen content from both oxides was controlled at the same level during the tests, the reaction time for the 3DOM $LaFeO_3$ would be shorter than that of the non-3DOM $LaFeO_3$. In an actual CLC or CLR process, a suitable degree of oxidation change during the redox cycles should be selected to obtain the desired reaction rate. Fully reducing the oxygen carrier to the theoretical reduced form, i.e., $X = 0$, is usually not necessary [23].

3.4.3. Methane oxidation performance

Isothermal methane oxidation tests were conducted in a fixed-bed reactor using the synthesized 3DOM $LaFeO_3$ perovskite as oxygen carrier. The gas product composition and H_2/CO molar ratio as a function of time are shown in Fig. 8. It is observed that the reaction initially proceeded to generate high concentrations of CO_2 (72.8%) with little CO and H_2 in the early stage. As the reaction proceeded, the CO_2 fraction decreased rapidly and closed to zero after 5 min, whereas the CO and H_2 fractions increased continuously and reached a plateau. CH_4 was apparently mainly oxidized to CO_2 and H_2O via total oxidation at the beginning of the reaction, and then was partially oxidized to H_2 and CO in the mid and later stages. As mentioned above, the oxygen species in perovskite-type oxygen carriers are classified into two types: surface adsorbed oxygen and bulk lattice oxygen [20]. Surface oxygen contributed to the complete oxidation of methane to CO_2 and H_2O because it has a higher reactivity. Lattice oxygen usually tends to partially oxidize CH_4 to H_2 and CO . Similar results have been reported by Wei et al [24] for $La_xSr_{1-x}MnO_3$ perovskites. It is clear that the higher degree of deep methane oxidation at the early stage was due to the surface oxygen species on the fresh oxygen carrier particles. As the surface oxygen species were depleted, lattice oxygen diffused from the bulk to the surface of the particles to cause selective methane oxidation, resulting in the observed increase of the CO and H_2 fractions. This explains why methane was oxidized to CO_2 and H_2O at the initial stage of the reaction and then selectively oxidized into CO and H_2 at later stages.

A low amount of unconverted methane fraction (9.2%) was

detected at the initial stage. The methane fraction increased dramatically at 1–4 min and then declined rapidly thereafter. This increase of methane concentration could be attributed to the release of bulk lattice oxygen in the oxygen carrier being too slow to compensate for the high rate of surface adsorbed oxygen consumption. After 7.5 min, the methane fraction remained at a low value of around 20%, and the fractions of H_2 and CO became stable in many of the reactions. The curve of the H_2/CO ratio shows that the H_2/CO molar ratio was around 2:1 before 20 min and then increased continuously to reach 6.5 at 24 min. It seems that part of the methane was decomposed to H_2 and C , which is verified by the fact that a small amount of CO_2 was detected at the start of the oxidation period. In our previous study, similar results were observed for the performance of non-3DOM $LaFeO_3$ perovskite in the partial oxidation of methane [15]. However, the concentrations of H_2 and CO were more stable during methane reaction with 3DOM $LaFeO_3$ than those with non-3DOM $LaFeO_3$. Moreover, the H_2/CO ratio remained around 2:1 for a longer time range with 3DOM $LaFeO_3$ than with non-3DOM $LaFeO_3$, indicating that 3DOM $LaFeO_3$ had a better performance for the chemical-looping reforming of methane than $LaFeO_3$ nano-powder.

The 3DOM structure of the present $LaFeO_3$ perovskite is expected to be beneficial to inhibit carbon deposition during reactions between carbonaceous fuels and oxygen carriers. The performance of carbon deposition suppression performance of the 3DOM $LaFeO_3$ perovskite will be reported in a future paper.

4. Conclusions

The vertical deposition method presented a more uniform and orderly PS template than those obtained by centrifugation and evaporation techniques. The perovskite synthesized with ethanol as precursor solvent exhibited better 3DOM structure than that produced with ethylene glycol solvent, while 1.0 mol/L may be the optimum precursor concentration. The obtained 3DOM $LaFeO_3$ was pure crystalline perovskite giving a surface area of 44.023 m^2/g , much higher than that of nano- $LaFeO_3$ powder (11.636 m^2/g) synthesized by a combustion method. The oxygen species in the 3DOM $LaFeO_3$ perovskite could be classified into two types: surface adsorbed oxygen and bulk lattice oxygen. The former contributed to oxidize methane completely to CO_2 and H_2O during the initial methane oxidation stage because of its higher reactivity, while the latter tended towards partial oxidation of methane to H_2 and CO in the mid and later stages. The multicyclic redox tests indicated that the 3DOM $LaFeO_3$ perovskite had good repeatability and released more oxygen than the same mass of non-3DOM $LaFeO_3$ during methane oxidation. The H_2/CO ratio remained around 2:1, which is suitable for gas-to-liquids processes, over a wide time range during methane oxidation.

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Graphical Abstract

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Synthesis of three-dimensionally ordered macroporous LaFeO₃ perovskites and their performance for chemical-looping reforming of methaneHE Fang*, ZHAO Kun, HUANG Zhen, LI Xin'ai, WEI Guoqiang, LI Haibin
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Three-dimensionally ordered macroporous LaFeO₃ perovskites exhibit better performance for chemical-looping reforming of methane than LaFeO₃ nano-particles because of their unique properties including high porosity and high specific surface area.

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三维有序大孔钙钛矿型氧化物LaFeO₃的合成及甲烷化学链重整性能何方^{a,*}, 赵坤^{a,b}, 黄振^a, 李新爱^a, 魏国强^{a,b}, 李海滨^a^a中国科学院广州能源研究所, 中国科学院可再生能源与天然气水合物重点实验室, 广东广州510640^b中国科学院大学, 北京100049

摘要: 采用无皂乳液聚合法制备了聚苯乙烯(PS)聚合物微球, 并采用胶晶模板法制备了三维有序大孔3DOM LaFeO₃钙钛矿型氧化物。通过扫描电镜、X射线衍射和傅里叶变换红外光谱等手段对氧化物的性能进行了表征。利用程序升温还原和多次氧化还原循环反应评价了氧化物的反应性, 并在固定床反应器上研究了其甲烷氧化性能。结果表明, 与离心法和蒸发法相比, 垂直沉积法获得的PS微球模板排列更均匀有序; 前驱物溶剂及浓度对最终的三维有序大孔材料的结构有显著影响, 利用乙醇为前驱物溶剂所制备的样品比利用乙烯为溶剂的样品具有更好的三维有序大孔结构, 前驱物乙醇溶液浓度在1.0 mol/L为宜。甲烷氧化实验表明, 3DOM-LaFeO₃钙钛矿型氧化物中存在两种氧物种: 表面吸附氧和体相晶格氧。表面吸附氧主要在反应初期将甲烷完全氧化为CO₂和水蒸汽, 而体相晶格氧主要将甲烷部分氧化为H₂和CO。在甲烷部分氧化反应中, 三维有序大孔LaFeO₃钙钛矿型氧化物比相同质量的纳米LaFeO₃氧化物提供了更多的氧, 并且可使甲烷在较宽的反应阶段生成H₂和CO摩尔比为2:1的合成气, 从而更有利于后续的费托合成等工艺。

关键词: 三维有序大孔钙钛矿氧化物; 氧载体; 合成气; 化学链重整; 甲烷

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