Liquid foam assisted sol-gel synthesis of iron oxides for hydrogen storage via chemical looping

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ABSTRACT

Chemical looping of iron oxides is capable of storing hydrogen with high capacity and low material costs. In this paper, we prepared iron oxides materials from the liquid foam templated sol-gel precursors and demonstrated its application in the chemical looping hydrogen storage process. By tuning the precursor chemistry, we obtained a series of materials with different pore configuration, and found this approach a convenient access to define the material configuration. With assistance of SDS, materials showed promoted porosity and better reactivity compared with the sample without SDS. In particular, samples with isolated pore structure were better able to limit the sintering. By characterizing the materials before and after cycles, we found the confinement effects of pore wall was capable of restraining the growth of the crystalline size, and thus mitigated the material deactivation in the high temperature redox cycles.

Keywords: Liquid foam; Oxygen carrier; Chemical looping; Hydrogen storage

1. Introduction

The stochastic nature of the wind energy input makes the large-scale energy storage technology an inevitable requirement. Using H₂ as a storage medium has been proposed as a promising method to address this problem, in which the electricity is fed in an electrolyzer, and then stored and carried

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as hydrogen. Currently, hydrogen can be stored physically in liquid or high-pressure state or chemically absorbed by a series of materials including hydrocarbons, metal alloys, metal hydrides as well as the currently active-developing carbon nanotubes and the metal organic frameworks (MOFs) [1-8]. Unfortunately, although significant progress has made on improving these materials, producing a high performance hydrogen storage material that combines good safety, high capacity with low manufacturing cost is still challenging.

An alternative technology capable of storing hydrogen is the chemical looping of iron oxides. [9-14]. In the first step, the pseudo-storage of hydrogen is realized by the reduction of the iron oxides oxygen carrier (OC). To maximize storage capacity (theoretically 4.8 wt.%), metallic iron is generally used as the nominal storage material.

Hydrogen charge:

Hydrogen discharge:

By recycling the water produced in the first step, the OC is then regenerated to its original state and simultaneously releases the stored hydrogen. In this process, one could note that the feedstock is only H_2O , Fe_3O_4 , which is readily available, environmentally friendly and very importantly, with low costs. Therefore, this technology may be promising in the application of large-scale hydrogen storage system, such as solar or wind plant where the hydrogen can be inexpensively produced from water [1,15-18].

However, there remain many challenges to successfully use this method to store hydrogen. One of the key challenges is that when using pure iron oxide, the process suffers from severe sintering of particles, caused by the high temperature cyclic operation of reduction and oxidation steps. This

implies that the practical hydrogen storage capacity will decay along with time. In the material science, sintering is susceptible to a number of influencing factors, including operating temperature, reaction atmosphere, promoters, material porosity, support species, *etc* [19-21]. Since this method was first proposed by Otsuka et al. [11], extensive studies have been performed on adjusting these parameters to limit the sintering. The mixing of some promoters, such as Cr, Ce, Rh, has been demonstrated efficient in lowering the reaction temperature, and thereby mitigates the sintering, mainly by Otsuka' group and Kim's group [9,11-13]. In some extreme cases, the operating temperature can be less than 300 °C, under which the sintering was negligibly slow but the kinetics of chemical looping is significantly limited. Dispersing the active component on refractory supports is an alternative way to limit the sintering with the material reduced and oxidized in high temperature. Currently, a number of supported OC has been prepared using various supports, including Al₂O₃, CeO₂, ZrO₂, TiO₂, yttria-stabilized zirconia (YSZ), MgAl₂O₄, *etc*, with different preparation methods, such as mechanical mixing, impregnation, co-precipitation, sol-gel, *etc*; the effects of support species, interaction of the support and iron oxides, dispersion of the cyclic phase, support loadings on the chemical looping performance are extensively studied in these works [22-32]. However, it is noticeable that changing the preparation conditions, *e.g.* support species, loadings, will inevitably lead to different pore configuration of the material, which was also reported as influential to the particle sintering. To be best of our knowledge, no such work concerning the effects of material porosity on chemical looping performance has been found to date.

Conventionally, the material porosity could be characterized as 2D or 3D structure configuration depending on the interconnectivity of the pores. Within the 2D matrix, the pores are one-dimensional and confined to the support surface. In such porosity, we can imagine that the

active component within a given pore can only interact with other particles in the same cavity, and has no opportunity to incorporate those in the neighboring pores. In contrast, the 3D pores possess the connecting channels between different pores, so the particles can circumvent the pore walls to interact with the components in the neighboring pores. At present, the effects of material porosity on the sintering have been carried out on the supported Au catalysts with a result showing that the sintering of Au particles is significantly affected by material pore size, pore wall thickness, pore connectivity, and pore strength. Datye and coworkers [33] found gold particles inside 3D pores with interconnecting channels sintered into larger ones more readily than did those inside 2D pores. At the same time, they observed smaller pores produced a smaller final particle size of the sintered nanoparticles than larger pores.

Apart from the impact on the sintering, it is well-known that the material porosity is important in the kinetics of the gas-solid reactions. For instance, the larger surface density of active sites can be generally achieved on the high specific surface of the micropores or mesopores, whilst macropores dramatically reduce the transport limitations and facilitate the mass flow. In addition, for a higher performance, the material should combine the macropores with mesopores, *i.e.* hierarchically organized and not just segregated pores [34,35].

The aim of this work is to investigate the effects of the material porosity on the OC performance in chemical looping hydrogen storage cycles. To obtain OC particles with different pore structure, we modified the conventional sol precursor with the assistance of liquid foam template. To figure out the precursor-structure-property relationship, we synthesized a series of OC particles by varying the surfactant SDS (sodium dodecyl sulfonate) amount and characterized the metal oxides with various physical and chemical techniques, and then we carried out the hydrogen charge and multicycles experiments to study the kinetics and the sintering of the prepared materials.

2. Experiments

2.1. OC preparation

The basic Fe-Al aqueous sol was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid (CA), polyethylene glycol (PEG, $M_w=400$) in the deionized water, followed by being heated in the oil bath at 60 °C with magnetic stir. The molar ratio of total metal irons, CA and PEG was set at 1:1:4 for the completely chelating and polymerizing the precursor during the sol-gel process. The loading of Fe_2O_3 in the final OC was designed at 75% in mass basis, according to the results obtained by Kidambi et al [22], where the preferable OC performance can be achieved.

The liquid foam template was synthesized by adding the surfactant SDS to the prepared sol with vigorous stir. By virtue of the amphiphilic effects of the surfactant, the continuous liquid phase and discrete gas phase can stably co-exist, forming large gas-liquid interface. Within the air-filled precursor solution, some of the surfactant micelles are swollen by the incorporation of bubbles to generate large pores, while the rest remain unswollen, producing small pores after template removal. The schematic diagram of the preparation of OC is shown in Fig. 1. The SDS amount added were calculated 10, 20, 30, 40 times as many as the critical micelle concentration (denoted as SDS-x, where x refers to the content of the surfactant), corresponding to SDS mass of 0.16, 1.59, 3.19, 4.78 and 6.37 g, respectively. The slurries were agitated with a magnetic mixer operated at 1000 rpm for 20 min to produce the foamed precursors. The gelation was induced by increasing the bath temperature to 95 °C for 8 h. Afterwards, the orange bodies were dried at 110 °C for 24 h, and then calcined in air atmosphere at 500 °C (2 °C/min ramp, 3 h dwell time) to crystalize the precursors and etch the template. Generally, the introduction of SDS could result in the residues of Na_2SO_4 after the template removal, which was reported as advantageous to the sintering due to its very low melting temperature (884 °C) [36], To eliminate the Na pollutant, the as-calcined particles were

washed in deionized water for three times, then the samples were dried and calcined (2 °C/min ramp to 900 °C, 3 h dwell time) again. Additionally, control samples prepared from the conventional precursor sols (without SDS) received the same treatment as the others, that is, soled, gelled, washed and crystallized.

2.2. OC characterization

The skeletal (ρ_s) and bulk (ρ_b) density were determined by MH-300A solid density apparatus. The open porosity (P) was calculated according to the relation $P = (1 - \rho_b/\rho_s)$. The porous structure was characterized by employing an Autopore III mercury porosimetry equipment (Micromeritics), and the corresponding pore diameter was calculated from the Washburn equation. A V-sorb X800 Surface Area and porosimetry Analyzer was used to perform the nitrogen adsorption-desorption analysis. In each measurement, 300 mg OC were evacuated at 250 °C for 5 hours prior to the measurement under 10 μ Pa of vacuum. The specific surface area of the samples was calculated following BET equation. To identify the chemical composition of the prepared OC, material powders were analyzed by an X-ray fluorescence spectrometer (XRF) system (ARL-9800). The morphology of the materials was examined using scanning electron microscopy (SEM). Materials, as-produced, were sputter-coated with a thin layer of gold and then imaged with a Hitachi SU3500 electron microscope. The crystalline phases were recognized using Powder X-ray diffraction (XRD) method on a Ultima IV diffractometer, where Cu, Ka radiation was generated at 30 mA and 40 kV, and the scanning scope (2theta) was in a range of 5° to 85°.

2.3. H₂ charge performance in TGA

TG analysis (TGA-ZRT1, JY GK) was carried out to evaluate the H₂ charge performance of five prepared samples. In each test, Fe₂O₃ was directly used without pretreated into Fe₃O₄ state; samples of 30 mg were loaded in a platinum pallet and heated to the desirable temperature (900 °C) at a

fixed heating rate of 10 °C/min. The reduction of the OC particles was performed using the mixer of 50 vol % N₂ and 50 vol % H₂ with a total flow rate of 40 ml/min, at STP. After each experiment, N₂ was purged for 10 min to sweep out the remaining gas in the reactor.

2.4. Cyclic performance in a fixed bed reactor

A fixed-bed reactor made of stainless steel with a total length of 400 mm and an inner diameter of 12 mm was used to perform the cyclic experiments. A porous distributor was installed at 180 mm from the bottom of the reactor to support the bed material. The heat was provided by an electric furnace and the reaction temperature was monitored and controlled by two thermocouples, one (T₁) was located between the tube and the furnace and another (T₂) was inserted into the OC bed material. By adjusting T₁, the desired T₂ could be reached, that is also considered as the reaction temperature.

The flow rates of N₂, H₂ (99.99% purity) were measured by the mass flow controllers (MFC, Beijing Sevenstar Co. Ltd). The distilled water was introduced by a high performance liquid Longer Pump (LSP01-2A, 0.166nl-10.831ml/min) and evaporated by steam generator operated at a constant temperature of 250 °C. Steam was conveyed into the reactor by means of a N₂ carrying gas with the heat taps operating at 250 °C to prevent the heat loss along the inlet tubes. The schematic layout of the experimental setup is shown in Fig. 2.

Prior to each experiment, 15 ml sand particles with a size range of 0.6-1.0 mm was placed on the porous distributor to prevent the OC particles from falling through the distributor. A batch of 3.4 g OC particles (0.075-0.125 mm) was subsequently loaded on the sand bed, after which the reactor was heated under the N₂ atmosphere. When the desired temperature (900 °C) was reached, the samples were alternately exposed to a reducing (200 ml/min H₂ and 100 ml/min N₂, at STP) and oxidizing (0.5 ml/min water and 100 ml/min N₂, at STP) atmosphere with 5 min N₂ purging (300

ml/min N₂, at STP) between each gas switching. The duration of the redox step was determined when the evolved gas composition kept constant.

The outlet gas was mixed with the diluting N₂ to accommodate the limited range of the Emerson multi-component gas analyzer, and then introduced to an ice-water cooler and a silica gel dryer successively. The gas analyzer has a detection range of H₂ (0-50%, 0.1% uncertain).

2.5. Data evaluation

(1) Volumetric flow rate of outlet hydrogen

The volumetric flow rate of outlet hydrogen was calculated based on a N₂ mass balance method:

$$V_{H_2} = \int_{t_1}^{t_2} V_{out} x_{H_2} dt \quad (3)$$

with

$$V_{out} = V_{N_2,in} / x_{N_2,out} = V_{N_2,in} / (1 - x_{H_2}) \quad (4)$$

where x_{N_2} and x_{H_2} are the detected concentration of N₂ and H₂ in the gas analyzer, V_{in} and V_{out} are the total inlet and outlet volumetric gas flow rate, respectively.

(2) Hydrogen storage capacity

The theoretical hydrogen storage capacity (R_x) for the OC was calculated by:

$$R_x = \frac{m_{Fe_3O_4} - m_{Fe}}{8m_{Fe}}$$

Where $m_{Fe_3O_4}$ and m_{Fe} are the theoretical weights of sample in the form of Fe₃O₄ and Fe, respectively.

The practically maximum hydrogen storage capacity (R_{max}) for the OC was determined based on the data from TGA analysis and can be calculated as

$$R_{max} = \frac{m_{Fe_3O_4} - m_{red}}{8m_{red}} \quad (5)$$

Where m_{red} are the OC weights after the completely hydrogen reduction in TGA.

To evaluate the loss in hydrogen storage capacity, the loss coefficient (η) was defined as:

$$\eta = \frac{R_x - R_{\max}}{R_x} \quad (6)$$

(3) Hydrogen storage conversion

Hydrogen storage conversion (P_0), indicating the degree of the sample deactivation, was denoted as:

$$P_0 = \frac{\int_{t_1}^{t_2} V_{\text{in}, \text{H}_2} - V_{\text{out}} x_{\text{H}_2} dt}{11200 m_{\text{red}} R_{\max}} \quad (8)$$

Where $V_{\text{in}, \text{H}_2}$ is the inlet H_2 volumetric flow rate, t_1 and t_2 are the starting and ending points in a charge process.

3. Results

3.1. Effect of SDS amount on the porous characteristics of OC

Due to the fact that SDS has the ability to define the bubble size distribution (Fig. 1), the microstructure of the final material can be efficiently controlled, that is, varying the micelles concentration in the precursor sols to realize the desired large and small size pore configuration. The feasibility of this approach is demonstrated by the results shown in Table 1. Clearly, when SDS added, the porosity was dramatically promoted with a maximum value of 87.3%, in which there was a 30% improvement in contrast to the OC without SDS. Comparing the different five samples, Table 1 also illustrates an optimal SDS concentration of 20*[CMC], under which the higher BET specific surface area and open porosity were provided. The reason of this result could be attributed to the different pore distribution in the material, as shown in Fig. 3. In the case of SDS-0, we can observe the pore distribution was similar to that without SDS. This indicated the major contribution of the surfactant was just to protect the incipient porous structure (which is produced by the polyesterification between CA and PEG) from significant shrinking in drying the gel. The ability of

SDS to adjust the pore structure was activated when the surfactant concentration reached over $20 \times [\text{CMC}]$. The result under which suggested SDS began to form regular micelles with some of them swollen by air, leading to the hierarchically small and large pores configuration. In geometry, this architecture could combine the higher BET surface area with good material porosity. However, instead of further promoting the material porosity, the increase of SDS concentration to $40 \times [\text{CMC}]$ adversely affected the material porosity, agreeing well with the findings by Beozzo et. al and Martins et. al [34,37]. On account of the large amount of carbon network formed in the precursors, serve coalescence of pores probably happened during the removal of the template, and thereby the BET surface area decreased.

Based on the porous characteristics of these five samples, the pore size can fall into three families, mesopore ($d < 0.01 \mu\text{m}$), supermesopore ($0.01 \mu\text{m} < d < 1 \mu\text{m}$), macropore ($d > 1 \mu\text{m}$). The corresponding mean pore sizes are calculated and revealed in the last three columns of Table 1. As can be seen, the samples prepared under lower SDS concentration present no macropores but meso and supermesopores. This porous structure may be a result of the shrink of the macropores by capillary tension during the thermotreatment process. The macropores occurred when SDS concentration reached $20 \times [\text{CMC}]$, implying a minimum surfactant amount under which the bubbles began to be incorporated into micelles. In these cases, we also detected the meso and supermesopores, and the pore sizes decrease when more SDS introduced. With respect to the production mechanism, especially mesopores, the slit cavities resulting from the non-parallel stacking of platelets could be responsible.

The representative SEM images (Fig. 4) confirmed the effect of SDS amount on the porous characteristics of OC. The morphology of samples without SDS showed the porous structure produced by the original polyesterification network. Fig. 4b illustrated the peak of the pore

distribution detected by Hg porosimetry (Fig. 3b) with morphology of uniform and isolated pore distribution. For the SDS-20 with the hierarchical pore configuration, the interconnectivity between the pores was observed.

3.2. H_2 charge performance in TGA

The hydrogen charge and discharge rates are important for a hydrogen storage technology; at present, previous work has confirmed the charge process is the rate-limiting step [38]. To enhance the charge kinetics, we have adjusted the pore structure by the liquid foam template sol-gel process. Using the prepared five samples, the kinetic study was performed in this section, and the effects of pore structure on the charge behavior were investigated.

The results from TG analysis are shown in Fig. 5. For these five runs, the OC conversion acted as a continuous increase and then stabilized at the maximum value with the time elapse. With the assistance of SDS, SDS-10, 20 and 30 showed the significantly promoted performance in kinetics. To be more specific, the OC conversion reached close to 30% in SDS concentration of 30*[CMC] that was in contrast to only 8% without SDS when the temperature increased up to 530 °C. However, the charge performances of SDS-40 come down even worse than SDS-0 with only 70% OC conversion when others prepared with SDS were fully converted. Two major reasons may be responsible for this result. One was the higher BET of SDS-10, 20 and 30 which indicated more gas-solid contact and therefore favored the charge reactions. Another was the more amounts of larger pores in the preferred samples. By virtue of the better mass transport in large pores, the fast diffusion of H_2O could be achieved within these materials, which thermodynamically favored the OC conversion according to Bauer–Glaessner diagram [30,39].

Owing to the addition of the support Al_2O_3 , the theoretical hydrogen storage capacity (R_x) is expected lower than 4.8% using pure Fe_2O_3 . The results, as shown in table 2, confirmed the loss in

hydrogen capacity due to the additives, *e.g.* the theoretical value dropped down to 3.16% for SDS-40. As can be seen from Table 3, we also found the Fe, Al contents were closed to the nominal value, and some contamination, mainly containing S, Na, Si, was mixed during the preparation process. It is worth noticing that all the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ mass ratios detected here was more than the nominal value of 3.0. This can be explained that a certain amount of Al and Na formed NaAl_2O_4 and was removed during the washing step.

Apart from the loss led by the dilution in Fe_2O_3 content, further deterioration in hydrogen storage capacity can be observed when comparing the theoretical hydrogen storage capacity (R_x) and practically maximum hydrogen storage capacity ($R_{\max}$). This loss was possibly due to the resultant close pores in the material, based on a fact that the sample possessing less open porosity (Table 1), lost more capacity consequently.

3.3. Charge and discharge behavior in a fixed bed

For the chemical looping with hydrogen storage, the cyclic material was cycled between Fe_3O_4 and Fe. However, we start from the OC in the state of Fe_2O_3 . So, the first charge and discharge cycle cannot be completely repeated because of the thermodynamically limitation in steam oxidizing Fe to Fe_2O_3 . Therefore, the chemical looping is repeated from the second cycle. For understanding the precursor transformation and the subsequent redox behavior using the prepared Fe_2O_3 OC, we conducted the first two cycles in this section, and performed a weakened reaction atmosphere (30 ml/min H_2 + 170 ml/min N_2 in reduction, at STP, 0.05 ml/min water + 100 ml/min N_2 in oxidization, at STP) to detail the evolution of outlet hydrogen.

Fig. 6 depicts the variation of outlet hydrogen as a function of reaction time. Initially, all the inlet hydrogen was absorbed by OC, suggesting the reduction between Fe_2O_3 to Fe_3O_4 . The exhaustion of the precursor Fe_2O_3 can be determined from the breakthrough of hydrogen at 5 min, the point at

which the thermodynamics was dramatically weakened because OC was in form of Fe_3O_4 or FeO [39]. With regarding to the subsequent evolution, a steady and mild increasing tendency was highlighted; this indicated the corresponding reduction was not processed at a strict stepwise sequence of $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ but simultaneously $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$. It was noteworthy that large amount of hydrogen were free to be charged due to the thermodynamic limited, implying the extensive energy and economic penalty. To increase the practical feasibility of this technology, recycling the off gas should be conducted. The principle of which is, cooling down the outlet products to enhance the hydrogen partial pressure over the equilibrium limit, and reendowing the gas mixtures with the chemical activity to react with OC.

For the discharge process, the hydrogen evolution can be characterized as an initial surge to the peak amount, indicating the chemical reaction was the rate-limiting step, and followed by exponential decay with the reaction progressing. The total amount of released hydrogen in this step was calculated as 893 ml, which was in contrast to 1022 ml in the charge step. The loss can be ascribed to the no contribution of the reduction of Fe_2O_3 to Fe_3O_4 to the steam-iron process. After the first discharge process, the later processes can be expected to circulate between Fe_3O_4 and Fe . As a result, initial increase in hydrogen signal was detected.

3.4. Cyclic performance of the prepared OC

In this section, 20 cycles were performed to evaluate the OC recyclability at 900 °C. Fig. 7 shows the variation of the relative storage potential along with the cyclic numbers. Obviously, the storage potential decayed rapidly in the first 15 cycles, indicating significant changes in material composition and structure, and then followed a relatively stable tendency. This result was in good agreement with the previous reports, of which two major reasons have been acknowledged [22,24,27,40,41]. Briefly, the Al_2O_3 supports can interact with OC to form a spinel composition of

FeAl_2O_4 . That implied the OC would lost partial active content irreversibly because the formed FeAl_2O_4 was thermodynamically stable even in hydrogen atmosphere (Fig. 9). Sintering was another important cause of the OC deactivation. Generally, it led to the shrink in BET surface area and growth in crystalline size, indicating less active oxygen accessible to convert the fuel (Table 4 and 5).

For the four testing samples, a big difference in the redox performance was observed although it had the same compositions. For example, SDS-10 maintained 80% potential after 20 cycles that was in contrast to only a half of SDS-40. Therefore, it was authentic that the pore structure played a pivotal role in the OC recyclability. As mentioned in the introduction, 2D pores without interconnectivity could restrain the particle interactions by the confinement effects of the pore walls. On the contrary, the 3D pores possessing connecting channels were more favorable to sintering due to the particle migration. As illustrated in table 5, the SDS-0 and SDS-10 with relatively isolated pore structure showed smaller crystalline size after 20 cycles, whereas the size of SDS-20 and SDS-40 with good pore interconnectivity grew over 100 nm. SEM imaging also confirmed the advantages of resisting the sintering for samples with 2D pores. By comparing the surface morphology before and after the redox cycles, we have found the sintering of SDS-10 was relatively slight. However, it is undeniable that the crystalline size of SDS-10 still doubled comparing with the fresh OC. As evident from SEM results, the destruction of the pore walls was probably a major culprit. The pore size distribution after 20 cycles (Fig. 10) further suggested the intimal pore structure can influence the evolution of the material microstructure, *i.e.* the sintering behavior. Comparing the four samples, we found SDS-10 with isolated pores possessed greater porosity after 20 cycles, whereas the other three lost most of the pores during chemical looping.

4. Discussions

4.1. Mechanism of sintering

In the case of our proposed process, two sintering mechanism, crystallite migration and atomic migration, were possibly involved. Crystallite migration involves the migration, collision and coalescence of entire crystallites within the support network. On the other hand, atomic migration, referred to as Ostwald ripening, involves detachment of metal atoms or metal clusters from crystallites, and then transportation from small particles to larger particles. Thermodynamically, Ostwald ripening would be accelerated at lower temperatures than crystallite migration, because of the higher diffusivities of atoms or small cluster. However, only if the temperature required for activating the migration of larger nanoparticles reached, crystallite migration may take place.

In our current work, we start with Fe_2O_3 particle size about 29 nm and operated the redox cycles in the temperature as high as 900 °C. Therefore, the crystallite migration was considered as a major contribution to sintering. Depend on our experimental results, the sample with isolated pores show preferred performance compared to others with 3D matrix. The confinement effect of the pores on the particle growth illustrates an approach of controlling the support structure to limit sintering. To attain higher performance, the strength of pore walls needs to be good enough to restraint the crystallite growth. On one hand, we could increase the wall thickness by promoting the support loadings. On the other hand, modifying the support with promoters, such as Ce, Ti, Zr, Mg, *etc*, to increase the pore strength is also viable practically.

4.2. Liquid foam template prepared material for clean energy applications

Similar to the chemical looping hydrogen storage process, many other novel processes for energy applications are dependent on the redox cycles of materials. Examples are chemical looping combustion [26], steam iron process [42,43], chemical looping gasification [44], calcium looping [45], and solar hydrogen production [46].

One of the major challenges involved in these processes are lack of a material with satisfactory activity because the conventional preparation methods, such as mechanical mixing, impregnation and coprecipitation, are hard to produce materials with good porosity after high temperature calcination. According to our current research, liquid foam template assisted sol-gel method can provide a convenient access to the desired pore structure of material, *i.e.* hierarchal porosity and high BET surface area. More importantly in high temperature cycles, sintering is of great concern. By carefully tuning the precursor chemistry, we successfully obtain the isolated pore structured Fe-based OC with better ability to resist the sintering. For other clean energy applications, we anticipate this strategy can be employed to produce more materials with both good activity and recyclability.

5. Conclusions

We reported the synthesis of iron oxides using liquid foam assisted sol-gel process and demonstrated its application in the chemical looping hydrogen storage process. By investigating the precursor-structure relationship, we found this method a convenient access to define the material pore configuration, *e.g.* the 2D or 3D pores can be obtained by just tuning the SDS concentration in the precursor sols. Among the five prepared samples, SDS-10, 20 showed better activities due to the promotions in the material porosity. Particularly, SDS-10 was better able to resist the sintering as well. By characterizing the materials before and after cycles, we confirmed the important role of pore structure in the material performance, and found the growth of the crystalline size could be limited by the confinement effects of pore walls. However, after high temperature redox cycles, the isolated pores can be interconnected when the pore walls destroyed, thus accelerating the sintering. We anticipate further work to increase the pore strength, aiming at developing better material for chemical looping or other clean energy applications.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China (Grant No. 51476035), National Science Foundation for Distinguished Young Scholars of China (Grant No. 51525601) and the Scientific Research Foundation of Graduate School of Southeast University (Grant No.YBJJ1609) for financial support of this project.

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Table captions

Table 1. Porous characteristics of the prepared OC.

Table 2. Hydrogen storage capacity of five prepared samples.

Table 3. Elemental analysis of the freshly-prepared OC by XRF, on oxide basis (wt%).

Table 4. BET analysis of the prepared OC obtained at typical cycles.

Table 5. Crystallite sizes calculated from XRD patterns using Rietveld analysis

Figure captions

Fig. 1. The schematic diagram of the preparation process of OC.

Fig. 2. Schematic diagram of the experimental setup.

Fig. 3. Differential pore size distribution of OC prepared under different concentration of SDS in the precursor solution.

Fig. 4. SEM images of the freshly prepared OC. (a) SDS-0; (b) SDS-10; (c) SDS-20; (d) SDS-40.

Fig. 5. TG analysis on the H₂ charge behavior of five prepared OC particles.

Fig. 6. The variation of outlet hydrogen as a function of reaction time using SDS-10 as a representative.

Fig. 7. The hydrogen storage conversion as a function of cycle number.

Fig. 8. SEM images of the OC after 20 cycles. (a) SDS-0; (b) SDS-10; (c) SDS-20; (d) SDS-40.

Fig. 9. XRD patterns of SDS-10 as a representative. (◆) Fe₃O₄; (▲) Fe₂O₃; (☆) FeAl₂O₄; (□) Al₂O₃.

Fig. 10. Differential pore size distribution of OC after 20 cycles.

Table 1.
Porous characteristics of the prepared OC.

sample	SDS concentration (mol/L)	Specific pore volume (cm ³ /g)	BET specific surface area (m ² /g)	Open Porosity (%)	$\bar{D}_{\text{meso}}$ (μm)	$\bar{D}_{\text{supermeso}}$ (μm)	$\bar{D}_{\text{macro}}$ (μm)
SDS-0	0	0.21	3.05	51.3	0.02	0.27	-
SDS-10	10*[CMC]	1.07	10.78	84.1	0.04	0.44	-
SDS-20	20*[CMC]	1.32	15.44	87.3	0.06	0.48	1.61
SDS-30	30*[CMC]	1.14	4.74	85.4	0.03	0.39	1.85
SDS-40	40*[CMC]	0.41	3.61	66.9	0.01	0.28	2.23

Table 2.
Hydrogen storage capacity of five prepared samples.

Sample	R_x (%)	R_{max} (%)	η (%)
SDS-0	3.15	3.09	2.04
SDS-10	3.14	3.10	1.52
SDS-20	3.15	3.08	2.46
SDS-30	3.14	3.01	4.38
SDS-40	3.16	2.94	7.18

Table 3.
Elemental analysis of the freshly-prepared OC by XRF, on oxide basis (wt%).

Sample	Fe ₂ O ₃	Al ₂ O ₃	Contaminates	Fe ₂ O ₃ /Al ₂ O ₃
SDS-0	73.66	24.49	1.85	3.008
SDS-10	73.49	24.38	2.13	3.014
SDS-20	73.64	24.21	2.15	3.042
SDS-30	73.51	23.88	2.61	3.078
SDS-40	73.73	23.44	2.83	3.145

Table 4.
BET analysis of the prepared OC obtained at typical cycles.

sample	BET specific surface area (m ² /g)		
	fresh	10 th cycles	20 th cycles
SDS-0	3.05	1.03	0.64
SDS-10	10.78	3.19	2.67
SDS-20	15.44	2.85	1.74
SDS-40	3.61	0.97	0.61

Table 5.
Crystallite sizes calculated from XRD patterns using Rietveld analysis

sample	Crystallite size (nm)	
	fresh	20 th cycles
SDS-0	39.5	87.1
SDS-10	29.0	62.9
SDS-20	21.4	>100
SDS-40	23.6	>100

Figure

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