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CO₂ Absorption of Powdered Ba₂Fe₂O₅ with Different Particle Size

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Abstract: Particle size dependence of CO₂ absorption rate of powdered Ba₂Fe₂O₅ with three kinds of particle size was studied by XRD, SEM, particle size distribution measurement and thermogravimetry. From the particle size distribution measurement, average particle sizes of the powdered Ba₂Fe₂O₅ samples were estimated about 52.5 μm, 77.5 μm and 100.0 μm, respectively. Results show that the reaction of CO₂ with Ba₂Fe₂O₅ was controlled by the diffusion step in the product layer, and the kinetics process could be described by the RPP model (Real Physical Picture). Moreover, Ba₂Fe₂O₅ exhibits a good recycling performance though the adsorption capacity is reduced slightly during the cycle processes, and the pathway of the CO₂ adsorption-desorption on Ba₂Fe₂O₅ has also been obtained, which suggested that Ba₂Fe₂O₅ is a promising CO₂ absorbent material.

Keywords: Ba₂Fe₂O₅, CO₂ captor, different particle size, adsorption-desorption

Introduction

Due to the industrial revolution, greenhouse gases caused by human beings increased year by year. So the atmospheric greenhouse effect is enhanced largely, thus causes a series of serious problems such as global warming, which attract global attention [1, 2,3,4]. Since carbon dioxide is the main component of greenhouse gases, looking for a suitable material to capture and store CO₂ is an important research subject. Different kinds of materials

have been proposed as CO₂ captors, for example polymeric membranes, zeolites, and different oxides [5, 5,6,7,8,9]. Nevertheless, all of these materials present one or more disadvantages. Hence, new materials for CO₂ capture must possess the following properties: high selectivity and sorption capacity for CO₂ at elevated temperatures, adequate absorption/desorption kinetics for CO₂, good recyclability for the absorption/desorption process, and good hydrothermal and mechanical properties [10, 11].

Ba₂Fe₂O₅, as a new CO₂ captor, was reported by Miyoshi [12], and the absorption is supposed to depend on the following reaction:

Compared with other CO₂ captors, Ba₂Fe₂O₅ has some outstanding properties. For instance, the CO₂ chemisorption of Ba₂Fe₂O₅ can be performed in a wide range of temperature, from 500 °C to 1100 °C. Moreover, it has been confirmed that the reaction (1) is reversible, that is, the reaction (1) progresses toward the right direction below 1100 °C, and the left direction over 1100 °C, which means that Ba₂Fe₂O₅ can be repeatedly used as a novel CO₂ absorbent. Fujishiro et al. researched that kinetics and mechanism of chemical reaction of CO₂ and Ba₂Fe₂O₅ under various CO₂ partial pressures [13], in addition, the reaction of CO₂ and Ba₂Fe₂O₅ should be influenced by the size of powdered Ba₂Fe₂O₅, but for now, relevant papers have not found. Multicycle property is also an important property for an outstanding CO₂ captor. Therefore, in this paper, we study particle size dependence of the reaction rate of the powered Ba₂Fe₂O₅ with three kinds of particle size and multicycle property by means of XRD, SEM observation, particle size distribution measurement, and thermo-gravimetric analyzer, and the kinetics process is also described by the RPP model (Real Physical Picture).

Experimental

Ba₂Fe₂O₅ samples were synthesized by the solid-state method using barium carbonate (BaCO₃, analytically pure) and ferric sesquioxide (Fe₂O₃, analytically pure). Initially,

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BaCO₃ and Fe₂O₃ powders were calcined at 150 °C for 10 h to remove the adsorbed water, and then they were weighed in the stoichiometric ratio of Ba₂Fe₂O₅ and mixed with ethanol in an agate mortar by hand for 1 h. After that, the mixture was pressed into a disk of 18 mm diameter at 0.4 GPa, and the disk was sintered on an alumina crucible at 1200 °C for 10 h in N₂ gas flow. The sintered disk was mechanically crushed into powder using an agate mortar, and then the gained powder is divided into three kinds of particle sizes by sieves of different particle size. By this procedure, Ba₂Fe₂O₅ samples with three kinds of particle sizes were obtained. The obtained samples were examined by XRD (Model, TTR III, Japan) to confirm whether the Ba₂Fe₂O₅ samples were single phase or not. Median particle size of the powdered Ba₂Fe₂O₅ samples was measured through particle size distribution (frequency distribution and accumulative distribution) by laser diffraction and scattering method.

The CO₂ absorption measurement was performed on these three powdered Ba₂Fe₂O₅ samples. For the measurement, about 20 mg of the powdered Ba₂Fe₂O₅ sample was used, respectively. The powdered Ba₂Fe₂O₅ sample was placed in the thermogravimetric instrument, where the experimental temperature raised to 1000 °C with a heating rate of 20 °C/min in N₂ gas flow, and then pure CO₂ gas flow with 50 mL/min was charged when the temperature reached 1000 °C to make the reaction take place in the CO₂ atmosphere until the sample mass reached constant. In this process, the thermogravimetric analyzer with sensitivity of 0.001 g was used to monitor the weight change of the powered Ba₂Fe₂O₅ sample continuously. In order to assess the reusability of Ba₂Fe₂O₅, the multicycle test was carried out. Ba₂Fe₂O₅ sample was first heated from room temperature to 1000 °C under a N₂ atmosphere, and then N₂ flow was switched to the CO₂ gas to start the adsorption reaction. After 2500 s, the sample was heated to 1200 °C with a heating rate of 20 °C/min and maintained this temperature for 1200 s to start the desorption reaction in a N₂ gas flow, then lowered temperature to 1000 °C at a rate of 20 °C/min. Then, the adsorption and desorption procedures were repeated. Scanning electron microscopy (SEM: Model S250MK3, CAMBRIDGE) was used to measure the morphology of the specimens before and after the TG measurement.

Results and discussion

Sample preparation

The XRD result of Ba₂Fe₂O₅ is presented in Figure 1, from which it can be seen that the pure Ba₂Fe₂O₅ can

Figure 1: X-ray diffraction patterns of Ba₂Fe₂O₅ and reaction products of Ba₂Fe₂O₅.

be prepared by BaCO₃ and Fe₂O₃ at the temperature of 1200 °C using solid-state method. And the reaction kinetics of Fe₂O₃ and BaCO₃ to prepare Ba₂Fe₂O₅ was studied in our previous paper [14]. SEM photograph of the Ba₂Fe₂O₅ sample is shown in Figure 2(a), from which it can be seen that the product is built by unregularly polyhedron-shaped and dense particles with sizes ranging within 1.0–3.0 μm. For the CO₂ absorption measurement, three kinds of powdered Ba₂Fe₂O₅ samples were prepared from the Ba₂Fe₂O₅ samples by the procedure mentioned under the experimental part. In order to measure average particle size of the three kinds of powered samples, particle size distribution measurement was performed on the powdered samples. Accumulative distribution and measured frequency distribution of the powdered samples are shown in Figure 3. According to the figure, it could be recognized that the frequency distributions of the samples look almost symmetry, and median particle sizes of the samples were measured that 52.5 μm, 77.5 μm and 100.0 μm, respectively. Because of symmetry of the frequency distribution, the median particle size would be equal to average particle size.

Figure 1 also showed the XRD of reaction products of CO₂ and Ba₂Fe₂O₅ that median particle size was 100.0 μm. From the figure, it can be seen that only BaCO₃ and BaFe₂O₄ appeared at the end of reaction. And the SEM of reaction products is shown in Figure 2 (b). It was found that secondary particles with diameters of 3–4 μm, which consisted of BaCO₃ and BaFe₂O₄, were observed on large raw particles, and they were dense and homogeneous.

Figure 2: SEM photographs of the Ba₂Fe₂O₅ sample and reaction products of Ba₂Fe₂O₅.

Rate analysis for the CO₂ absorption

Weight change of the powdered Ba₂Fe₂O₅ samples was measured with reaction time t at a target reaction temperature T by the thermogravimetric instrument. As a typical example of the estimation, reaction extent ($\Delta m_t / \Delta m_0$, Δm_t is the quality increase at time t , Δm_0 is the theory maximum quality increase) was plotted to the

reaction time t at 1000 °C for the samples with 52.5 μm, 77.5 μm and 100.0 μm of the particle sizes in Figure 4. From the figure, it is found that, first, reaction extent linearly increases with a constant slope in the first 180 s and the slopes of the three curves are almost equal, then from 180 s, the slopes of the three curves began to appear different. So it can be concluded that the reaction rates begin to differ after 180 s, and the reaction extent of the powdered samples with smaller particle size rises in shorter reaction time, that is, the CO₂ absorption reaction seems to progress in shorter reaction time. But the slopes decrease with the increase of reaction time. The difference of slopes means that progression of the CO₂ absorption reaction seems to be disturbed by some kind of factor. The longer the reaction time of Ba₂Fe₂O₅ and CO₂ gas is, the thicker the products (BaCO₃ and BaFe₂O₄) phases formed on Ba₂Fe₂O₅ particle are, which will disturb the progression of the CO₂ absorption reaction. Therefore, the reaction is more and more difficult to proceed with the CO₂ absorption reaction proceed gradually. And a tendency is found that the slopes decrease with the increasing particle size.

Chou model

The reaction between CO₂ and Ba₂Fe₂O₅ firstly begins from the surface of the Ba₂Fe₂O₅ particle, and the layer of BaCO₃ and BaFe₂O₄ becomes thicker and thicker. Therefore, the rate of the whole reaction will be controlled by the diffusion in the product layer.

Chou et al. [15–17] have succeeded in establishing a RPP (Real Physical Picture) model to describe the kinetics

Figure 3: Accumulative and frequency distributions of the powdered samples, (a) 52.5 μm, (b) 77.5 μm (c) 100.0 μm.

Figure 4: CO₂ adsorption curves under various particle sizes at 1000 °C.

of reaction controlled by the diffusion process in the solid-product layer, as shown in eq. (2), which is a form of explicit function, so the RPP model is easy to use and enable the easy performance of theoretical analysis.

$$\xi = 1 - \left(1 - \frac{1}{R_0} \sqrt{\frac{t}{B_{R_0}}} \right)^3 \quad (2)$$

and

$$\xi = 1 - \left(1 - \frac{1}{R_0} \sqrt{\frac{t}{2328474849522.17}} \right)^3. \quad (4)$$

$$B_{R_0} = \frac{1}{\left(2K_{CO_2}^{o\beta} D_{CO_2}^o / v_m \right) \left(\sqrt{P_{CO_2}} - \sqrt{P_{CO_2}^{eq}} \right) \exp \left(- \frac{\Delta \varepsilon + \Delta H}{RT} \right)}, \quad (3)$$

where R_0 is the radius of the original whole particle, B_{R_0} is a function of T , P_{CO_2} and $P_{CO_2}^{eq}$, in which $P_{CO_2}^{eq}$ is the carbon dioxide partial pressure in equilibrium with oxide and should be related to the temperature; $K_{CO_2}^{o\beta}$ and $D_{CO_2}^o$ are constant independent of temperature; B_{R_0} will be constant as the temperature and the carbon dioxide partial pressure are fixed. Equation (2) is the formula representing the effect of particle size on the reacted fraction from which it may be seen that the smaller the particle size, the larger the reacted fraction. It is because the particle with a small radius has a larger surface and thus a faster reaction rate. Note that particle size has the most effect on the reacted fraction in comparison with the other two factors, temperature and oxygen partial pressure.

The reaction kinetics of CO₂ and Ba₂Fe₂O₅ in isothermal can be described by eq. (2). Figure 5 shows the fitting results, and it can be seen that the experimental data and theoretical predicted values are in good agreement which validates the present theoretical approach. The model describing the effects of particle size and time on the reacted fraction is given as follows:

Multicycle property of Ba₂Fe₂O₅

The multicycle performance of Ba₂Fe₂O₅ in the conditions of adsorption in CO₂ gas (1000 °C) and desorption (1200 °C) in N₂ gas is shown in Figure 6. It can be seen from Figure 6, Ba₂Fe₂O₅ exhibits a good recycling performance though the adsorption capacity is reduced slightly during the cycle processes.

The produced powders of different stages of reaction were characterized SEM analyses by Fujishiro [18]. The morphologies of the specimens at various reaction stages were observed to evaluate the CO₂ absorption mechanism. After heating for different temperatures, three types of specimens with reaction ratio of 0.3, 0.5, and 0.9 were obtained by Fujishiro. It can be seen that the as-prepared Ba₂Fe₂O₅ was composed of particles with diameters of 50–70 μm. As the reaction proceeded, secondary particles with

Figure 5: A comparison between experimental data and theoretical predictions from the RPP model.

Figure 6: The multicycle performance of Ba₂Fe₂O₅ in the conditions of adsorption in CO₂ gas and desorption in N₂ gas.

diameters of 5–7 μm, which consisted of BaCO₃ and BaFe₂O₄, were observed on large raw particles. Figure 7 (a) and 7(b) show the sample SEM images after 1 and 5 times adsorption–desorption cycles, respectively. Compared with the SEM images of adsorbed samples, it can be noticed that the morphologies of the samples after adsorption–desorption test are quite different, and it can be observed that the particles are flawed and loosed, which due to the release of CO₂ in desorption stage. Based on the above analysis, the pathway of the CO₂ adsorption–desorption on Ba₂Fe₂O₅ can be obtained and

shown in Figure 8. At the initial stage of adsorption, the BaCO₃ and BaFe₂O₄ external shell are formed on the surface of Ba₂Fe₂O₅, and as the reaction proceeded, the unreacted center Ba₂Fe₂O₅ is smaller and smaller until completely react. At the desorption stage, BaCO₃ reacts with BaFe₂O₄ to generate Ba₂Fe₂O₅ and CO₂, which makes Ba₂Fe₂O₅ flawed and loosed. The multicycle processes of adsorption–desorption take place between the flawed and loosed Ba₂Fe₂O₅ and BaCO₃, BaFe₂O₄.

Conclusions

Particle size dependence of CO₂ absorption rate of the powdered Ba₂Fe₂O₅ with three kinds of particle size was studied by XRD, SEM and TG. From the particle size distribution measurement, average particle sizes of the powdered Ba₂Fe₂O₅ samples were estimated about 52.5 μm, 77.5 μm and 100.0 μm, respectively. From the comparisons of measured kinetic curves with calculated results, it can be concluded that diffusion in the Ba₂Fe₂O₅ product is the rate-controlling step of the reaction of CO₂ with Ba₂Fe₂O₅. And the RPP model was well used to describe the reaction kinetics of CO₂ and Ba₂Fe₂O₅ in isothermal conditions. The good cycle characteristics show Ba₂Fe₂O₅ is an outstanding CO₂ captor.

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Figure 7: The sample SEM images of 1 (a) and 4 (b) times adsorption-desorption cycle.

Figure 8: The CO₂ adsorption-desorption pathway of Ba₂Fe₂O₅.

References

- [1] M.S. Kwak, J.S. Hwang, C.O. Park, N. Miura and N. Yamazoe, *Sens. Actuators B*, 56 (1999) 59–64.
- [2] E.J. Karlsen, M.A. Nygren and G.M. Pettersson, *J. Phys. Chem. B*, 107 (2003) 7795–1802.
- [3] J.W. Dijkstra and D. Jansen, *Energy*, 29 (2004) 1249–1257.
- [4] X. Wei, X. Liu and M. Deeba, *Appl. Catal. B: Environ.*, 58 (2005) 41–49.
- [5] S.K. Wirawan and D. Creaser, *Micropor. Mesopor. Mat.*, 91 (2006) 196–205.
- [6] E. Ocho-Fernández, M. Rønning, T. Grande and D. Chen, *Chem. Mater.*, 18 (2006) 1383–1385.
- [7] A. Macario, A. Katovic, G. Giordano, F. Iucolano and D. Caputo, *Micropor. Mesopor. Mat.*, 81 (2005) 139–147.
- [8] K. Nomura, K. Tokumitsu, T. Hayakawa and Z. Homonnay, *J. Radioanal. Nucl. Chem.*, 246 (2000) 69–74.
- [9] Z. Yong and A.E. Rodrigues, *Energy Convers. Manage.*, 43 (2002) 1865–1876.
- [10] N.D. Hutson, S.A. Speakman and E.A. Payzant, *Chem. Mater.*, 16 (2004) 4135–4143.
- [11] Z. Yong, V. Mata and A.E. Rodriguez, *Sep. Purif. Technol.*, 26 (2002) 195–205.
- [12] T. Miyoshi, Y. Saito and Y. Fujino, *Japan Patent Kokai P2007-296422A* (November 15, 2007).
- [13] F. Fujishiro, K. Fukasawa and T. Hashimoto, *J. Am. Ceram. Soc.*, 94 (2011) 3675–3678.
- [14] J.H. Liu, G.H. Zhang and K.C. Chou, *High Temp. Mater. Proc.*, 33 (2014) 319–323.
- [15] K.C. Chou, Q. Li, L. Lin, J. Jiang and K.D. Xu, *Int. J. Hydrogen Energ.*, 30 (2005) 301–309.
- [16] K.C. Chou and X.M. Hou, *J. Am. Ceram. Soc.*, 92 (2009) 585–594.
- [17] K.C. Chou, *J. Am. Ceram. Soc.*, 89 (2006) 1568–1576.
- [18] F. Fujishiro, Y. Kojima and T. Hashimoto, *J. Am. Ceram. Soc.*, 95 (2012) 3634–3637.