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Studying the removal of CO_2 on stratified ZnO prepared by hydro

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ABSTRACT

In this study, ZnO was synthesized by the simple hydrothermal method. The physicochemical properties of the materials were characterized by SEM, XRD, N adsorption/desorption isotherm methods. The CO_2 removal experiments were conducted using the thermogravimetric method (TGA). The material has a stratified structure, with a surface area of 24.4 m^2/g and a pore volume of 0.280 cm^3/g. The influences of temperature, ZnO morphology, and feed gas composition were studied. Besides, the durability and applicability of the material were evaluated through repeated regeneration.

Introduction

Currently, we are facing a series of pressing environmental problems on the global including climate change, degradations of biodiversity, freshwater resources, ozone layer, and soil, and pollution of toxic and persistent organic substances. These issues are interrelated and all directly affect human life as well as social development. In particular, whether at the national or global level, climate change is always considered the hottest environmental issue, moreover, it is also considered an important issue affecting the process of sustainable development, currently worldwide. Scientists have reached a high consensus that socio-economic development activities scaled up in many fields such as energy, industry, transport, and agriculture, and forestry in recent decades have increased the concentration of greenhouse gases (N_2O, CH_4, CFCs, H_2S, and especially CO_2) in the atmosphere, warming the Earth leading to climate change [1].

Scientists and countries have been trying to find alternative energy such as solar and wind energies. However, Scientists and countries are trying to find alternative energy such as solar and wind energies. But, fossil energy still contributes a large proportion to global energy, it cannot be completely replaced by other sources, currently. A large amount of CO_2 and other harmful gases emitted from factories and engines need to be removed before being released into the environment [2].

Metal oxides have been proved to be effective materials for CO_2 adsorption from flue gases. Magnesium oxide synthesized from supercritical and precipitation method could adsorb CO_2 at a temperature less than 100 °C [3, 4], it could absorb CO_2 at medium temperature (250-400 °C) when the metal salt Alkali was added to MgO, the adsorption capacity is up to over 50 wt.% [5]. Calcium oxide can absorb CO_2 at high temperatures (>600 °C) with an adsorption capacity that can reach 40 wt.%, but the desorption temperature needs to be above 800 °C [6].

There are many studies on ZnO for CO_2 reduction and detection [7-9], there are still few studies on CO_2 absorption on ZnO.

In this study, we focus on preparation of stratified ZnO for CO_2 capture at low temperature (<150 °C). ZnO was synthesis by facile precipitation method. As-prepared samples were characterized by SEM, XRD, BET, FT-IR and TGA. The effect of temperature on sorption of CO_2 was investigated. In addition, the stability of sample was investigated via cyclic experiment: Pure CO_2 sorption and N_2 thermal regeneration.

Experimental

Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99.5%) and urea $(NH_2)_2CO$, 99.5%) were purchased from China. N2 (99.99%) was used as a purge gas during activation and regeneration in cyclic test. CO_2 (99.99%) was applied for sorption test. The double distilled water was used through the experiments.

Synthesis of stratified ZnO

The stratified ZnO nanostructure was prepared by a simple hydrothermal process. In a first stage, 30 mL of zinc nitrate hexahydrate 0.5M, 0.03 mole of urea, and 70 mL of distilled water were put in a 250 mL beaker. The mixed solution was stirred at 240 rpm for 30 min. Then, the mixed solution was transferred into a Teflon-lined autoclave and heated at 90 °C for 24 h. Subsequently, the autoclave was cooled to room temperature, the precipitation was detached by vacuum pumping filtration, washed with distilled water for 4-5 times and dried at 90 °C for 24 h. Finally, the hierarchical flower-like ZnO nanostructures were obtained by calcining the precipitate at 400 °C for 2 h with a heating rate of 2 °C/min.

To compare the influence of morphology on CO_2 adsorption, the nanospheres, nanorods, and roses ZnO samples were synthesized according to previous publication [10], the CO_2 adsorption experiments were conducted in similar conditions to stratified ZnO.

Characterization

The crystalline phase of sample was investigated by X-ray power diffraction (XRD). XRD patterns were obtained by using Bruker D8 Ax XRD-diffractometer (Germany) with Cu Kα irradiation (40kV, 40 mA). The 2θ ranging from 10 to 90° was selected to analyses the crystal structure. The morphology and size of the samples were observed field emission scanning electron microscopy (FE-SEM, JEOL-7600F). Textural properties were measured via N2 sorption/desorption isotherms using a Quantachrome instrument (Autosorb iQ, version 3.0 analyzer). The specific surface area, pore volume and pore diameter were obtained by using the Brunauer-Emmett-Teller (BET) method.

TGA measurement

TGA, Versa Thermal Instrument), as seen in Figure 1. The TGA system (Versa Thermal Instrument) has a temperature range up to 1000 ºC, a capacity of 1.0 gram, a sensitivity of 0.2 ug and an accuracy of 0.1%. The balance operates on a null-balance principal using a highly sensitive transducer couple o a tout-band suspension system to detect minute change in the mass of sample.

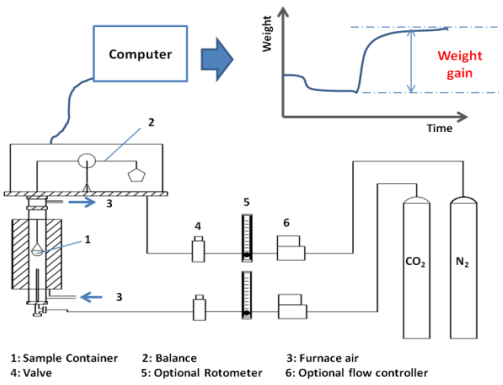

Figure 1: TGA structure and process

Typically, an amount of samples 0.1 g was put in the sample container. Before the CO_2 sorption, the as-prepared samples were activated at 450 °C in N_2 flow of 30 mL/min for 1 h, the activated temparature was slightly higher than calcination teperature to remove moisture, solvents, other adsorbates and complete decompostion of impurity $ZnCO_3$ in the samples due to adsorption of CO_2 during experiments. The sample was then cooled to sorption temperature and the N_2 flow gas was changed by CO_2 of 20 mL/min. The mass of adsorbent increased due the sorption of CO_2, when it approached saturation the weight gain was contributed to CO_2 adsorbed on the sample and it was evaluated by following equation.

$$CO_2 \text{ uptake } (\%) = \frac{Sorbed\ CO_2\ weight\ (g)}{Sorbent\ weight\ (g)} \times 100\ (\%) \quad (1)$$

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Result and discussion

Characterization of materials

Figure 2 shows the characterization of as-synthesized ZnO. The ZnO sample was observed as the stratified structure with uniformly flower approximately of 10-15 µm in size, as shown in Figure 2(a). The micro flower-like ZnO was composed of many nanosheets formed by many zinc oxide nanoparticles, as shown in Figures 2(b). The crystal phase of the samples was characterized by XRD analysis and the result is displayed in Figure 2(c). The diffraction peaks of the precursor before calcination were in good agreement with zinc hydroxide carbonate, $Zn_4(CO_3)(OH)_6.H_2O$ (JCPDS:11-0287), while the diffraction peaks of calcined hydrothermal product were attributed to ZnO (JCPDS:19-1458)[11] and no other peaks for impurities were detected, indicating the precursor was completely transformed into the pure ZnO at calcination temperature of 400 °C for 2 h. The isotherm and pore size distribution curves of ZnO sample are presented in Figure 2(d). The surface area and pore volume of as-synthesized ZnO were 24.4 m^2/g and 0.280 cm^3/g, respectively.

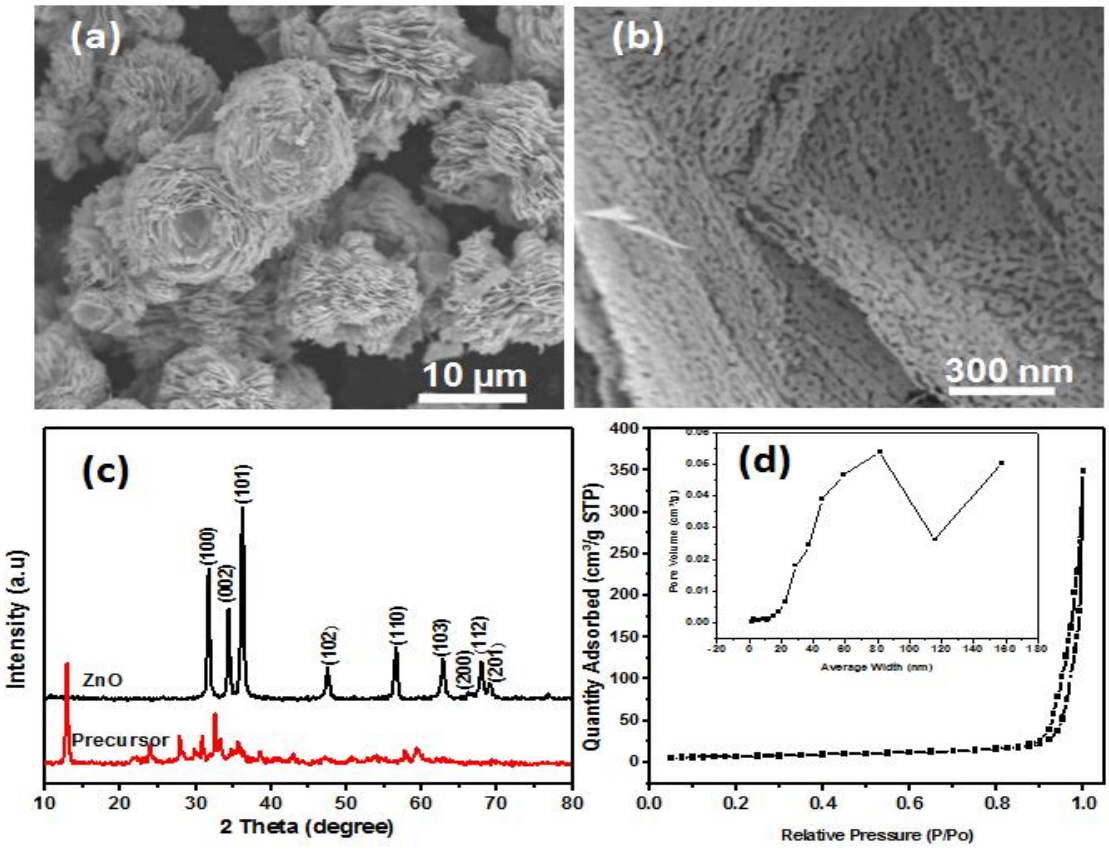

Figure 2: (a-b) SEM images of stratified ZnO with different scale bars; (c) XRD patterns of the precursor before calcination and as-synthesized ZnO; (d) N_2 adsorption/desorption isotherm (inset: pore size distribution) of as-synthesized ZnO

Adsorption experiment

Effect of temperature on CO_2 adsorption

CO_2 adsorption on stratified structure ZnO was studied in the temperature range of 25-150 ^oC, results are presented in Figures 2 and 3. It was clearly seen that temperature has a great influence on the adsorption of CO_2. When the temperature increased, the adsorption was decreased. The adsorption capacity reached about 90% at the initial 15 min and reached saturation in 120 min.

The adsorption capacities at 25 °C for 15 and 120 min were 5.91 and 6.86 wt.%, respectively. These values were decreased as the adsorption temperature increased, showing 1.78 and 2.27 wt.%, respectively, at 150 °C.

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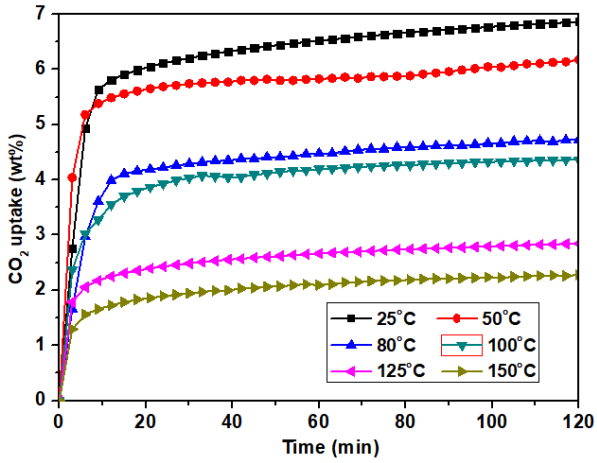

Figure 3: CO_2 uptake on ZnO at different temperatures and 1 bar

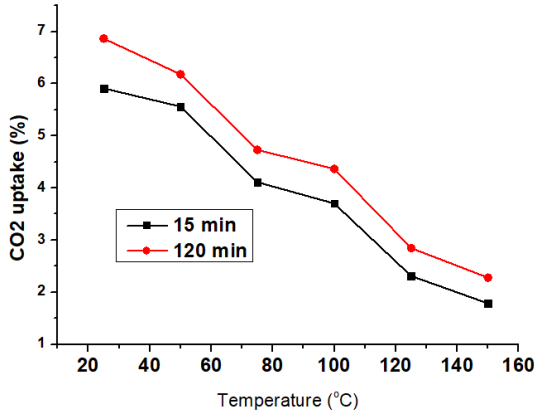

Figure 4: CO_2 uptake on ZnO at 15 min and 20 min for different temperatures

Effect of the morphology of ZnO on CO_2 adsorption

To study the influence of morphology on the adsorption efficiency of CO_2 on a material, ZnO with different morphologies such as nanospheres, nanorods, and roses ZnO samples were synthesized according to the previously report [10]. The surface area of sample were showed in Table 1. The results are presented in Figure 5. The CO_2 adsorption on ZnO nanorods increased gradually with time, exhibiting an adsorption capacity of 4.47 wt.% in 120 min. The adsorption tended to slightly increase after 120 min. The adsorption rate of ZnO nanospheres in initially 30 min was lower, but its adsorption capacity was smaller than those of ZnO roses. The adsorption capacities were 6.51 and 6.33 wt% for ZnO nanospheres and ZnO roses, respectively. Meanwhile, ZnO stratified structure exhibits the fastest adsorption rate compared to other morphologies, its adsorption capacity in 120 min was 6.86 wt%. However, the adsorption capacity per surface area of roses ZnO was higher than those of other samples. Thus, not only the structure but also the surface area affected the CO_2 adsorption of ZnO materials.

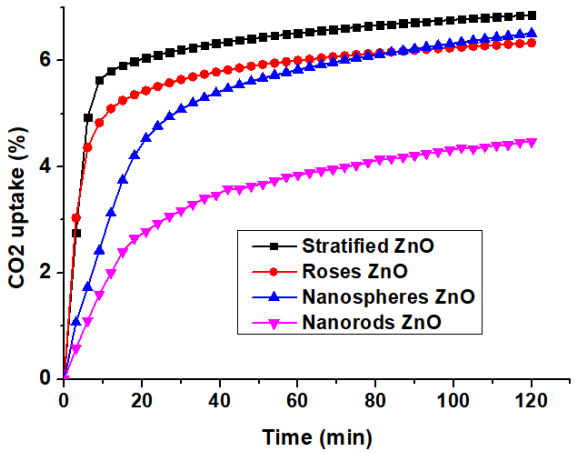

Figure 5: Effect of morphology on adsorption of CO_2

Table 1: Surface area and adsorption capacity per surface area

Sample	Surface area (m^2/g)	Adsorption capacity per surface area (mg/m^2)
nanospheres ZnO	26.4	2.47
nanorods ZnO	18.1	2.47
roses ZnO	16.1	3.93
stratified ZnO	24.4	2.81

Effect of CO_2 concentration of adsorption

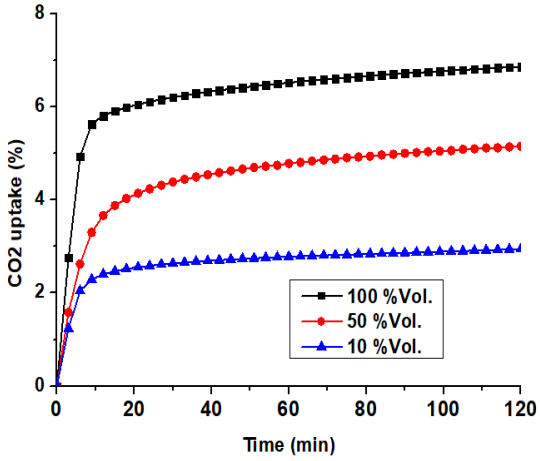

Figure 6: Effect of feed gas component on CO_2 adsorption

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Because the concentration of CO_2 from factory exhaust is about 10 % vol. In this study, the effect of CO_2 content on the adsorption capacity of ZnO was studied in the range of 10-100 %Vol. The results are presented in Figure 6. We see that, when the CO_2 content was reduced, the adsorption capacity of ZnO was lowed. However, the adsorption rate was in the first stage then reached saturation at 120 min. The adsorption capacity reached about 90% in the initial 15 min for all experiments.

Table 2: Comparision of CO_2 adsorption on other ZnO samples form references

Samples	Adsoprtion capacity (mg/g)	Reference/this work
NPs ZnO	17.6	[12]
ZnO/C-S-L	142.1	[13]
MgO-ZnO composites	35	[14]
Stratified ZnO	68.6	This work

There were many applications of ZnO for the determination of CO_2 and catalyzing for the conversion of CO_2 to methane and methanol, but researches on the adsorption of CO_2 on ZnO were few. The comparisons of CO_2 adsorption on ZnO and their composite materials are shown in Table 2. It was found that the CO_2 adsorption capacity of ZnO was higher than those of ZnO MgO-ZnO composite NPs but was smaller than that of the ZnO/C-S-L sample.

Cyclic sorption capacity and stability

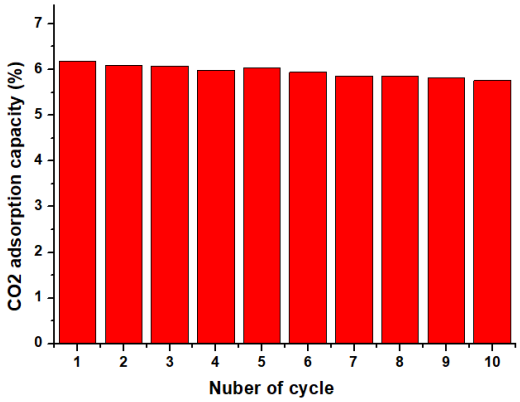

Figure 7: Cyclic test temperature profile and sorption capacity of ZnO operated by sorption at 25 °C and regeneration at 400 °C; pure CO_2 sorption and N_2 regeneration

The as-synthesized ZnO showed fast sorption, which reached about 90% of saturation capacity within 15 min at 25 °C, in Figure 3. With respect to the reproduce of CO_2 capture, fast cyclic operation is desirable. However, in the study, CO_2 sorption/desorption cyclic tests were conducted under accelerated test conditions (long sorption and desorption times) to evaluate the stabilities of the as-synthesized ZnO. Pure CO_2 sorption was conducted 25 °C for 15 min, and N_2 flow regeneration was performed at 400 °C for 30 min to complete decomposition of $ZnCO_3$, as shown in Figure 7. ZnO showed relatively stable for CO_2 adsorption. The sorption capacity of ZnO at tenth cycle was 5.67 wt%, which was 94.6 % of the capacity at the first sorption. In addition the surface area of stratified ZnO sample after tenth regeneration was 22.6 m^2/g. This demonstrates that ZnO was stable at activated temperature of 450 ^oC and at regeneration temperature of 400 ^oC for 10 times and it could be a potential material for application in CO_2 capture.

Conclusion

The stratified ZnO was successfully synthesized by a simple hydrothermal method for CO_2 adsorption. As the temperature increased, the CO_2 adsorption capacity was decreased. The adsorption capacity at 25 °C was 6.86 wt.%. ZnO has a better CO_2 adsorption capacity than other forms such as nanospheres, nanorods, and roses. The CO_2 content in the feed gas affected the adsorption rate and capacity. However, the adsorption still rapidly approached 90% saturation in the first 15 min and reached saturation in 120 min. Research results have demonstrated that ZnO was stable and could regenerate many times for CO_2 capture. It will be a potential material for application in remove CO_2 from emission sources.

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