

Synthesis of mesoporous cerium compound for CO₂ capture

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Abstract. A mesoporous adsorbent was simply synthesized by adding alkaline substances to cerium(III) nitric hydrate. The surface characteristics of the synthesized cerium compound were determined with BET, XRD and TEM analysis. It was found that although the specific surface areas of the synthesized cerium compounds were among about 120–200m² per gram (BET area) which were smaller than the common used zeolite 13X (BET area 743 m²/g) and activated carbon (BET area 1079 m²/g), but the cerium compounds had excellent performances for CO₂ adsorption as well as the CO₂ desorption.

1 Introduction

Many investigations have shown that carbon dioxide (CO₂) emissions are responsible for climate change. So many advanced countries have promoted the reduction of CO₂ emitted from large stationary sources including coal-based power plants, steel industry plants, biogas plants, and chemical plants. The development of both economical and environmental benign ways to separate and storage the CO₂ has become a global challenge. Two major approaches have been implemented as CO₂ separation technology: carbon dioxide capture/sequestration (CCS) and sustainable utilization of captured CO₂ as a raw material. The latter will play an important role within the next decade because CO₂ is a non-toxic, abundant, easily available, and renewable carbon resource that can be converted into various useful chemical products. A state-of-the-art process for capturing CO₂ from largely exhausted flue gases has been developed by employing amine-based, regenerative chemical absorption using aqueous amines. This process has a high efficiency for CO₂ capture, but it is energy intensive, complex and requires a high-energy input for regenerating and handling the corrosive solvents that result from the oxidation of amine-based solutions.

Compared with the conventional amine-based absorption, a process for capturing CO₂ using novel solid adsorbents capable of energy-efficient reversibility is far more advantageous. In this regard, various porous materials with fine structural and chemical properties have been widely investigated including zeolites, activated carbon, amine-modified silica materials, and metal organic frameworks. Those materials have been

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practical candidates that allow us to perform pressure swing adsorption (PSA) and temperature swing adsorption (TSA) processes for CO₂ capture from a variety of large emission sources.

Many studies have suggested that synthetic zeolites and amine-modified mesoporous materials could be applicable for CO₂ capturing in the post-combustion flue gas with low concentration of CO₂ and low pressure region. Chaikittisilp and Jones have reported that amine-modified mesoporous materials were effective for the CO₂ capturing from dilute CO₂ containing flue gas (< 10%) under ambient condition [1]. Yu and Cheng succeeded in the fabrication of amine-functional porous silica microspheres, which showed good CO₂ adsorption-desorption performance under high temperature flue gas condition (in the range of 348–383 K) with excellent cyclic stability [2]. These novel porous materials may be useful under some conditions, though, the conditions of flue gases (CO₂ concentration, pressure, gas components, etc.) may sensitively limit the range of applications, thereby adsorbents must be selected appropriately according to the target emission sources. For instance, the high pressure gasification process may exhaust high concentration of pre-combustion CO₂ gas with an elevated pressure. Capturing the CO₂ from high pressure flue gases would profit in terms of energy-efficiency in the PSA process, thus the adsorbents should be suitable to capture sufficient amount of CO₂ under high pressure region. Current PSA adsorbents such as zeolites and amine-modified mesoporous materials may not be most suitable materials for capturing high concentration of CO₂ under high pressure condition. Activated carbon still shows low durability against water vapour whereas mesoporous carbon materials specially designed for CO₂ capture is also high cost.

In this study, we focused on the use of metal oxides with larger true densities than other porous materials, in particular, we considered cerium compounds such as cerium oxide and cerium hydroxide as an alternative, efficient adsorbent for the CO₂ capture process. Cerium oxide, known as ceria, has been a subject of thorough investigations, and has attracted a lot of attention mainly in the field of catalysts and catalytic supports [3]. Many attempts have been made to improve the catalytic activity of ceria by enhancing its thermal stability and surface area with ordered porous structures. However, the practical application of ceria to CO₂ capture has not been fully investigated even though conventional ceria has the potential to adsorb and desorb the CO₂ under ambient conditions owing to its strong Lewis-base sites [4].

In order to develop a high efficient cerium compounds adsorbents for capturing CO₂, the primary interest is to enhance the surface area of cerium compounds. Several approaches have been proposed for increasing the surface area. These approaches include the soft-templating method using poly-block copolymers or organic structure-directing agents, the hard-templating method, which usually replicates the ordered mesoporous structures from SBA-15, KIT-6 or MCM-48, the self-assembly of surface modified ceria nanoparticles, and supercritical drying under CO₂ conditions. The above methods provide ways to enhance the surface area of ceria to around 200 m²g⁻¹. However, these processes are complex, high cost and high energy consumption. Therefore, a simple synthesis route is desirable for the production of high surface area ceria from both industrial and environmental standpoints.

In this study, we tried a simple preparation of mesoporous cerium compounds with a high surface area of up to 206 m²g⁻¹. The mesoporous ceria was prepared based on the so-gel method, where the product was simply precipitated within a short reaction period at room temperature under optimized synthesis conditions. Compared with the commercially available non-porous ceria, zeolite 13X, and activated carbon, the prepared mesoporous cerium compounds showed the results with high performance of CO₂ adsorption-desorption.

2 Experiments

2.1 Simple synthesis of mesoporous cerium compounds without template

The following raw materials were used as provided: using sodium hydroxide or ammonia as alkali sources and cerium (III) nitrate 6-hydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Kanto Chemical Co., Ltd) as the cerium source. To compare the CO_2 adsorption capacity of the cerium products, commercially available non-porous ceria, typical activated carbon and zeolite 13X were used as reference materials.

The mesoporous cerium compound samples were synthesized by the following procedure: cerium (III) nitrate 6-hydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to ethanol (99.5% $\text{C}_2\text{H}_5\text{OH}$, Kanto Chemical Co., Ltd) and stirred for 2h to obtain a colloid (A). NaOH was mixed with distilled water with various $\text{OH}/\text{H}_2\text{O}$ ratios. Then the $\text{NaOH}(\text{B})$ solution was added to the A and mixed thoroughly using a magnetic stirrer at room temperature until the suspension became faint yellow. The resulting solution was then separated with a centrifugation. The sediment product was washed with distilled water until it approached a neutral pH and thereafter dried at room temperature in a vacuum desiccator over one night.

2.2 Characterization

The wide-angle powder X-ray diffraction (XRD) patterns of the solid products were collected by a powder X-ray diffractometer (Ultima IV, Rigaku Corp.). The crystalline morphology and crystal size of the products were observed using a transmission electron microscope (TEM, H-7650, Hitachi High-Technologies Corp.) with an accelerating voltage of 100kV. The pore characteristics of the samples were evaluated by performing N_2 adsorption-desorption measurement using an automatic gas adsorption apparatus (3 Flex, SHIMADZU Corp.). To evaluate the surface areas, the Brunauer-Emmett-Teller (BET) method was applied. The pore size distribution curves were calculated with the Dollimore-Heal (DH) method.

2.3 CO_2 capturing experiment

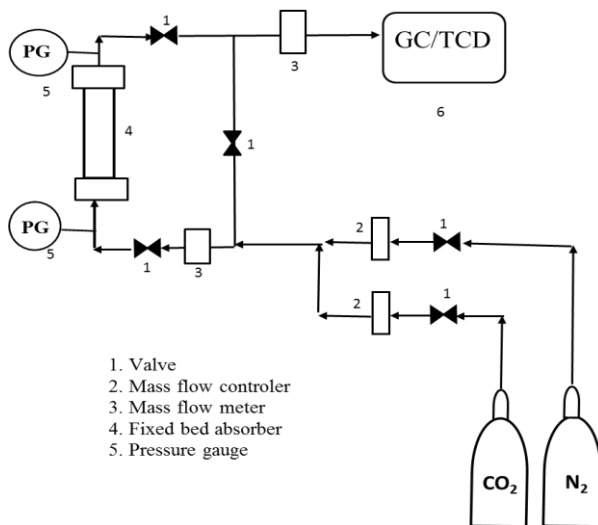
A simplified schematic diagram of the experimental setup is shown as Figure 1. The experiments were carried out under a pressure of 0.1, 0.5, 1.0, and 1.5 MPa respectively, at room temperature. The sample amount was fixed to 3.0g. Before adsorption operates the system was purged with pure N_2 gas for 1h. The concentrations of CO_2 in the input and output were determined by GC/TCD (GC-8A, SHIMADZU Corp.) The capturing capacities for CO_2 were calculated by the following equation.

$$Q \text{ (mmol/g)} = \frac{V \times 44}{22.4} \left[\frac{\int_0^t (C_0 - C_t) dt}{m} \right] \quad (1)$$

where Q is the CO_2 capturing capacity, mmol/g; V is the flow rate of the gas, L/min; m is the weight of the adsorbent sample, g; t is the adsorption time, min.; C_0 and C_t is the CO_2 concentration in the input and output, respectively.

2.4 Adsorbent regeneration performance evaluation

The best synthesized sample (Sample No. 2) and zeolite 13X were selected to carry out circulating adsorption-desorption experiments to compare their regenerating performance. For each cycle, at first, the adsorption experiment was carried out at 298 K, under 1.0 MPa. When the adsorption reached the saturating point, the pressure in the reactor was released to atmospheric pressure, and then the reactor was purged with pure nitrogen gas for 1 hour to desorb the captured CO₂. The adsorption /desorption circulating experiments were carried out 10 cycles for each sample.



Temperature	K	298
Pressure	MPa	0.1, 0.5, 1.0

Fig. 1. Fixed-bed adsorption system for CO₂ adsorption-desorption experiments.

3 Results and discussion

3.1 Material synthesis and characterization

3.1.1 Synthesis of mesoporous cerium compound

During the stirring, the colour of the precipitate suspension changed from brown to faint yellow as shown in Figure 2.

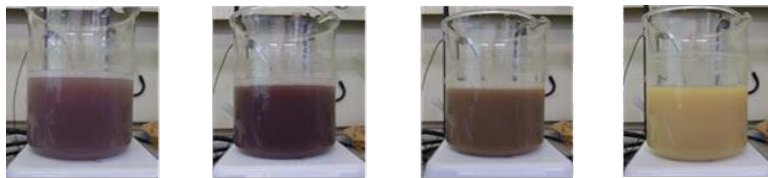
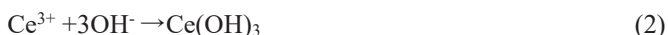


Fig. 2. The color change of the precipitate suspension for the sample with continuous stirring.

The reaction process could be explained as follows: at the initial stage of the reaction, hydrolyzed $\text{Ce}(\text{NO}_3)_3$ mixed with NaOH formed $\text{Ce}(\text{OH})_3$



here, the color of the aqueous suspension was turned into purple due to the presence of $\text{Ce}(\text{OH})_3$ species. When the reaction was further proceeded, the color eventually turned into faint yellow color, and the precipitation of CeO_2 obtained. Thus at the latter stage of the reaction, most of $\text{Ce}(\text{OH})_3$ formed during hydrolysis-condensation subsequently by the following oxidation step with the oxygen in the air,



The mesoporous ceria was synthesized based on sol-gel chemistry at room temperature in highly alkaline solutions with several different NaOH concentrations (see Table 1).

Table 1. BET surface area, total pore volume, average crystallite size of the products obtained.

Sample No.	Synthesis condition		S_{BET} ($\text{m}^2 \text{g}^{-1}$)	PV ($\text{cm}^3 \text{g}^{-1}$)	d (nm)
	Alkali	M (mol L^{-1})			
1	NaOH	0.11	152	0.29	5.9
2	NaOH	0.22	206	0.21	3.0
3	NaOH	0.28	182	0.34	3.6
4	NaOH	0.42	190	0.42	4.1
5	NaOH	0.84	191	0.41	3.7
6 (calcinated at 873K for 10 h)	NaOH	0.22	20	0.03	10.3

M : mol concentration of aqueous solution; S_{BET} : surface area calculated using BET method; PV : pore volume obtained from the volume of N_2 ; d : the average crystallite size evaluated from Scherrer's equation.

Table 1 shows that synthesis of the cerium compound by 0.22 M NaOH solution obtained a sample with highest surface area up to $200 \text{ m}^2 \text{g}^{-1}$, and the average crystallite size evaluated by Scherrer's equation was the smallest. The surface area of this sample is excellent comparing with those reported by literature references.

3.1.2 XRD analysis

Figure 3 shows the results of wide-angle powder XRD measurements of the synthesized solid products and a commercially available ceria (non-porous ceria). The obtained broad XRD patterns of the products were identified as pure crystalline ceria with six noticeable

peaks located at $2\theta = 28.5^\circ, 32.6^\circ, 47.1^\circ, 55.8^\circ, 68.7^\circ,$ and 76.5° , which can be indexed to the (111), (200), (220), (311), (400), and (331) reflections [4], respectively. For the product obtained by 0.22M NaOH, after it was calcinated at 873 K, the peak intensity greatly enhanced. The crystallite size of the calcinated ceria greatly increased from 3.0 nm to 10.3 nm owing to the further crystal growth of ceria induced by the calcination at high temperature.

3.1.3 TEM morphological features

The morphological features as well as particle sizes were observed by TEM. The TEM images of three synthesized samples are shown in Fig. 4. It is noticed that synthesized products were clearly agglomerates composited by fine particles. The shapes and sizes of the particles depended upon the concentration of alkaline solution.

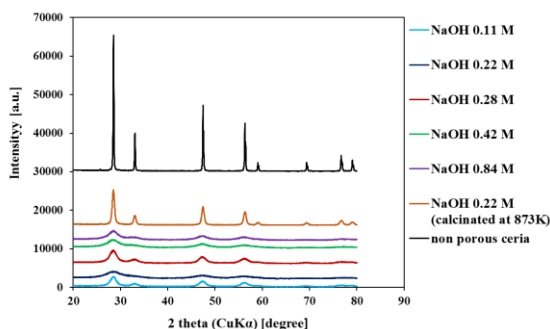


Fig. 3. XRD patterns of ceria synthesized with NaOH.

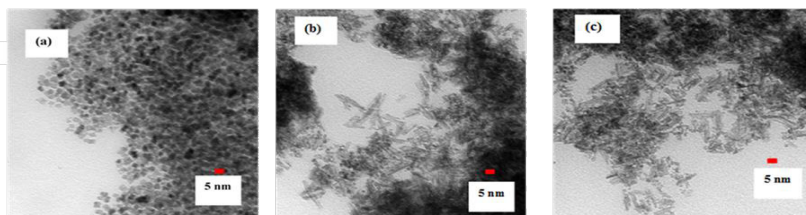


Fig. 4. TEM images of ceria synthesized with NaOH. (a) Sample no.2 (NaOH 0.22 M), (b) Sample no.3 (NaOH 0.42 M), (c) Sample no.4 (NaOH 0.84 M).

3.1.4 Pore size distribution

The pore size distributions of the synthesized products were obtained by nitrogen adsorption/desorption isotherms calculated using the Dollimore Heal (DH) method (see Fig.5). Except the sample obtained by 0.22M NaOH, which gave a sharp distribution for the pore size, all the samples gave broad distributions for pore size which covered the meso-porous region.

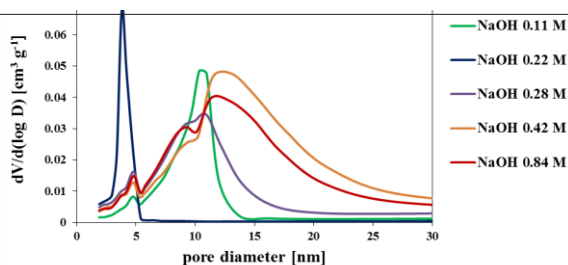


Fig. 5. Pore size distribution of ceria calculated using the Dollimore Heal (DH) method.

3.2 CO₂ capture

3.2.1 CO₂ capturing capacity

The CO₂ capturing capacities of the best synthesized product as well as commercial available adsorbents were compared shown on Fig.6, and their surface areas and pore sizes shown on Table 3. Although the surface area of the synthesized ceria (non-calcinated) is smaller than both the zeolite 13X and activated carbon, it had more excellent CO₂ capturing performance especially under high pressure.

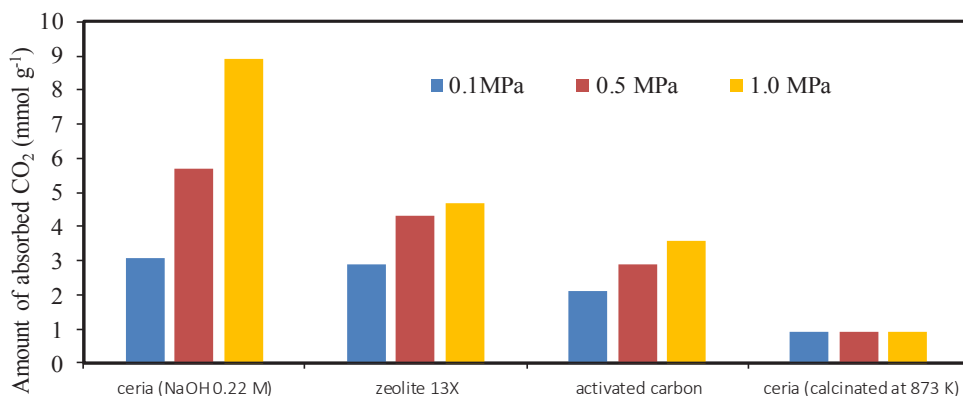


Fig. 6. Capturing capacities of adsorbents for CO₂ (298 K, 0.1MPa, 0.5 MPa, 1.0 MPa).

Table 3. Compare of amount of CO₂ capturing capacities among the different adsorbents.

Sample	S_{BET} ($m^2 g^{-1}$)	PD (nm)	Amount of adsorbed CO ₂ (mmol g ⁻¹)		
			0.1 MPa	0.5 MPa	1.0 MPa
Ceria (NaOH 0.22 M)	206	3.8	3.1	5.7	8.9
zeolite 13X	743	1.0	2.9	4.3	4.7
activated carbon	1079	2.9	2.1	2.9	3.6
Ceria (calcinated at 873 K)	20	4.0	0.9	0.9	0.9

3.2.2 Regeneration

Circulating adsorption-desorption experiments were carried out using the synthesized cerium product (sample No. 2) and comparing with the zeolite 13X. The results of CO₂ capturing capacities after operating up to ten cycles are shown on Fig. 7. From the experimental results, it can be concluded that the synthesized cerium product has not only a high adsorption capacity for CO₂ capture at room temperature under a high pressure condition, but also the good regenerating performance at room temperature under atmospheric pressure. Therefore, mesoporous ceria compound may be available a high efficient and energy-saving adsorbent for CO₂ PSA-capture from flue gas under a high pressure.

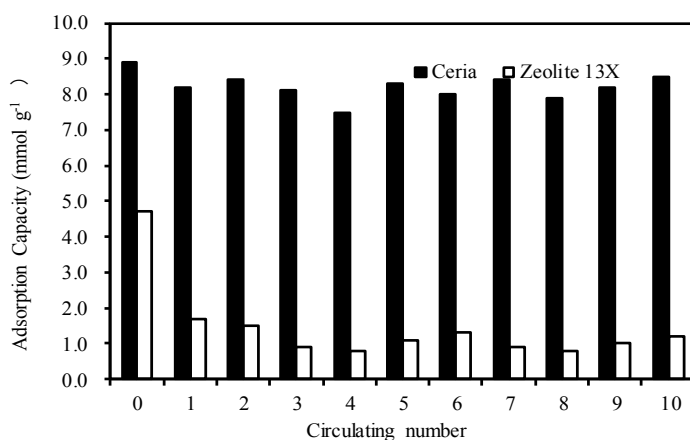


Fig. 7. CO₂ adsorption- desorption circulating tests at 298 K in the pressure range of 0.1 MPa ~1.0 MPa.

4 Conclusion

A high performance mesoporous cerium compound as the adsorbent for CO₂ capture has been successfully synthesized based on sol-gel method without template. The morphologic features and the porous characteristics of the synthesized cerium compound products are significantly affected by the concentration of alkaline solution added to the hydrolyzed Ce(NO₃)₃ to obtain Ce(OH)₃. Although the surface area of the synthesized cerium compound product (even though the largest one was up to 206 m²g⁻¹) is smaller than that of the commercially available zeolite 13X and activated carbon, the synthesized products have higher adsorption performance than the commercial adsorbents especially under higher pressure. Because of its excellent desorption performance at room temperature and under atmospheric pressure, the synthesized mesoporous cerium compound is promising for CO₂ capture with the pressure swing adsorption (PSA) process as a high performance adsorbent.

References

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