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Rapid One Pot Synthesis of Mesoporous Ceria Nanoparticles by Sol-gel Method for Enhanced CO_2 Capture

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The capture and storage of CO_2 have been suggested as an effective strategy to reduce the global emissions of greenhouse gases. Hence, many studies have been carried out to develop highly efficient materials for capturing CO_2. Herein, the CO_2 capture performance of mesoporous ceria nanoparticle (MCN) was described. The MCN was synthesized under mild conditions through a sol-gel method using hexadecyltrimethylammonium bromide (CTAB) as a surfactant and further undergone a calcination process at 673 K for 3 h. The prepared MCN possess high surface area (76.0 $m^2 g^{-1}$) which is around 9-fold higher than that of commercial CeO_2 (8.7 $m^2 g^{-1}$), indicating that the organic modification using CTAB is an effective way of preparing a porous structure. The MCN exhibited high CO_2 uptake of 213.8 μmol g^{-1} at 298 K and 1 bar. The prepared MCN using sol gel has shown a rapid and cost-effective method compared to the hydrothermal method.

1. Introduction

Global warming is recognized as the critical issue which recently affected the physical environment, social and economic developments (Miphokasap, 2017). Over the past decades, global warming has been identified as a climate threat due to the enormous amount of CO_2 released towards the atmosphere. CO_2 capture and sequestration (CCS) technologies have been considered as an effective choice to reduce CO_2 emission as a response to the climate change and to its devastating effects on human society and planet (Frontera et al., 2017). Typical liquid amines such as monoethanolamine (MEA) and diethanolamine (DEA) through chemical absorption in industry consist of several disadvantages such as low absorption capacity, corrosion issues, depleting solvent and high regeneration cost (Yu et al., 2012). These drawbacks can be reduced by adsorption process by synthesizing porous solid adsorbents structure with an excellent textural properties (Sreenivasulu et al., 2015). These includes high surface area, tunable pore structure, decent chemical/thermal stability and surface functionalization (Ji et al., 2016). For instance, Chowdhury et al. (2015) has reported the potential of mesoporous TiO_2/graphene oxide nanocomposites on CO_2 capture. The adsorbent exhibited a CO_2 uptake capacity of 1.88 mmol g^{-1} at room temperature, which is higher than many other commonly used adsorbents. Meanwhile, Lakhi et al. (2017) has developed a highly ordered mesoporous carbon nitrides with uniform rods for CO_2 capture that showed a high specific surface area and the large pore volume leading to high CO_2 uptake capacity of 15.4 mmol g^{-1} at 273 K and 30 bar.

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In this work, mesoporous ceria nanoparticle (MCN) was prepared via sol gel method based using hexadecyltrimethylammonium bromide (CTAB) as a surfactant. CTAB is used in order to create a highly surface area of mesoporous CeO_2 which mitigated the low surface area problem of commercial CeO_2 adsorbent. Prior to that, the best preparation conditions were obtained by hydrothermal method by varying the calcination temperature, pH values and Ceria/Surfactant ratios. The MCNs obtained have been thoroughly characterized by N_2 adsorption-desorption isotherms and thermal gravimetric analysis (TGA). The CO_2 adsorptions were applied at 298 K and 1 bar. The results obtained from this study indicates that MCN prepared via sol-gel method has a potential to be utilized as one of the promising, simple and low-cost adsorbents in CO_2 capture technology from the flue gas emission sources.

2. Methodology

2.1 Preparation of adsorbents

The MCNs were prepared via sol-gel and hydrothermal method. For hydrothermal method, an aqueous ammonia solution (10 mL of NH_3, 28 wt%) was added dropwise into solution of Ceria/Surfactant ratio of 2.0 and stirred for 30 min till the gelatinous purple solid was observed. The solution was then sealed in a glass vessel and placed in a thermostatic bath at 363 K for 3 h under continuous stirring. The as-synthesized adsorbent was dried at 383 K overnight and calcined at 673 K for 3 h. The studies on the effect of calcination temperature (673 K, 723 K, 773 K, and 823 K), pH value (1, 5, 7, 9 and 11), and Ceria/Surfactant ratio (0.5, 1.0, 1.5, 2.0) on the preparation were also done using hydrothermal method. The preparation steps of sol-gel method were similar to the hydrothermal method except the gelatinous pale-yellow solution was observed after premixing and the solution was stirred at room temperature for 1 h afterward.

2.2 Characterization and CO_2 adsorption technique

2.2.1 N_2 adsorption-desorption isotherms

The nitrogen adsorption–desorption isotherms were obtained using a physisorption analyzer (Quantachrome Autosorb-1) at liquid nitrogen. Prior to adsorption, the samples were outgassed at 573 K for 3 h for each measurement. The specific surface area was assessed using the BET method and the mesopore size distributions were analyzed using the Barrett–Joyner–Halenda (BJH) method.

2.2.2 Thermogravimetric analysis

Thermal gravimetric analysis (TGA) (Mettler Toledo TGA/SDTA 851e instrument) with a derivative weight loss curve was used to tell the point at which weight loss is most apparent. A set of parameters were set such as heating 12 mg sample with nitrogen stream at 1150 K with temperature ramp of 10 K min^{-1}.

2.2.3 CO_2 capture measurement

The CO_2 adsorption isotherms were measured using a Micromeritics Accelerated Surface Area Porosimetry System (ASAP 2020) volumetric adsorption analyzer at 298 K. Prior to each adsorption experiment, the sample was degassed for 2 h at 373 K and then cooled down to 298 K, followed by the introduction of CO_2 into the system. The CO_2 adsorption capacity in terms of adsorbed volume under standard temperature and at pressure range 6-900 mmHg was recorded.

3. Results and Discussions

3.1 Effect of calcination temperature on MCN preparation

The textural properties of all MCNs are shown in Table 1. As the calcination temperature decreased from 823 K to 673 K, the surface area and pore volume of the MCN were increased from 28.1 m^2 g^{-1} and 0.1048 cm^3 g^{-1} to 67.5 m^2 g^{-1} and 0.1802 cm^3 g^{-1}. Meanwhile the pore size decreased from 23 nm to 11.5 nm. The best calcination temperature was observed at 673 K (MCN-673) due to large surface area and pore volume with small pore size.

Figure 1a shows the N_2 adsorption-desorption isotherm of typical type IV curves with steep H1 small hysteresis loop in the relative pressure (P/P_0) range of 0.8-1.0. The location of the inflection point is related to the pores at the mesoscale, and the sharpness of these curves reveals the uniformity of the mesopore size distribution (Aziz et al., 2014). The isotherm of all samples exhibited large N_2 uptake around P/P_0 = 0.9-1.0, which indicates the presence of mesopores. MCN-673 had the highest steepness compared with others indicating that the sample possessed more mesopores than others. In general, all adsorbents displayed a bimodal pore structure consisting of framework mesopores at range 3-5 nm, and 10–60 nm (Figure 1b and 1c). Narrow distributions were observed around 4.0 nm for all the MCNs. However, significant distribution can be seen for MCN-773 around 20 nm while others showed relatively small distributions range from 18 nm to 50 nm.

Table 1: Textural properties of MCNs with different calcination temperature prepared via hydrothermal method

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
MCN-823	28.1	0.1048	23
MCN-773	37.2	0.1636	16.9
MCN-723	45.9	0.1911	13.6
MCN-673	67.5	0.1802	11.5

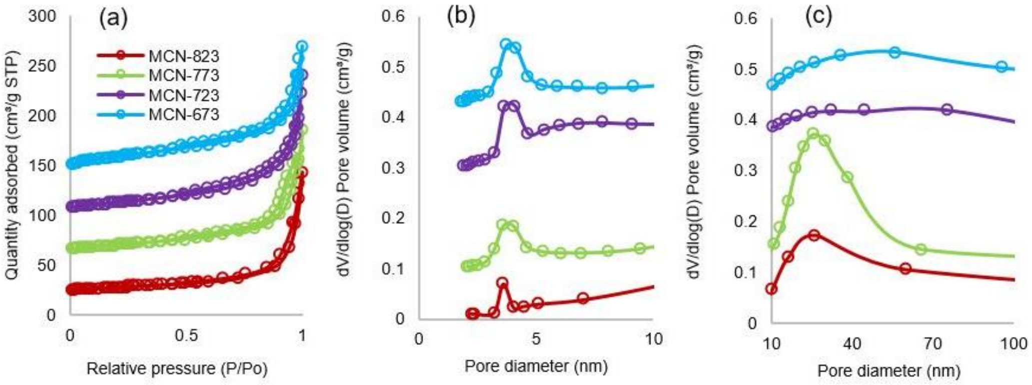

Figure 1: N2 adsorption-desorption graphical data for MCN adsorbents; (a) N2 adsorption-desorption isotherm for all samples, (b) pore diameter range from 0-10 nm MCN, (c) pore diameter range from 10-100 nm for MCN

3.2 Effect of pH on MCN preparation

The effect of pH on the properties of MCN is shown in Table 2. For pH 1 and pH 5, the preparation solutions were not form into cloudy condition due to acidic state. Therefore, the samples were not obtained in powder form. MCN synthesized at pH 9 shows highest surface area (43.8 m^2 g^{-1}) followed by at pH 7 (39.8 m^2 g^{-1}) and pH 11 (28.1 m^2 g^{-1}). In terms of pore size, as the pH value reduced from 11 to 9, the pore size reduced from 22.9723 nm to 14.0809 nm. Unfortunately, as pH was lowered to 7, the pore size increased significantly to 18.2850 nm. The pH 9 is the best pH value for the preparation of adsorbent because of the optimum level of the alkali added with surface area of 43.8 m^2 g^{-1}.

Table 2: Textural properties of MCNs. All samples were prepared by hydrothermal method with different pH values and calcined at 673 K.

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
MCN (pH 11)	28.1	0.1048	22.9723
MCN (pH 9)	43.8	0.1804	14.0809
MCN (pH 7)	39.8	0.1686	18.2850
MCN (pH 5)	-	-	-
MCN (pH 1)	-	-	-

Nitrogen sorption isotherms of the MCN in Figure 2a shows type IV curves with a steep H1 hysteresis loops, which indicates an agglomeration of uniform spheres with a complex mesoporous solid (Aziz et al., 2017). MCN (pH 9) had the highest steepness and MCN is the lowest steepness. At relatively low pressure of less than 0.5, the adsorption uptake was small, whereas an abrupt increase in adsorption uptake was seen in the relatively high pressure of more than 0.5 till 1.0. This could be considered as an indication of pronounced capillary condensation that took place in mesopores. A small hysteresis loop at relative pressures 0.8 to 1.0 was ascribed to the condensation of nitrogen within interstitial voids or to the interparticle textural porosity created by MCN particles, indirectly reflects the size of particles that is, a bigger partial pressure was affiliated with a smaller particle size (Aziz et al., 2018). The inflection points were similar but the MCN (pH 9) had the highest sharpness of the steeps indicating most uniformity of micropores of the adsorbent.

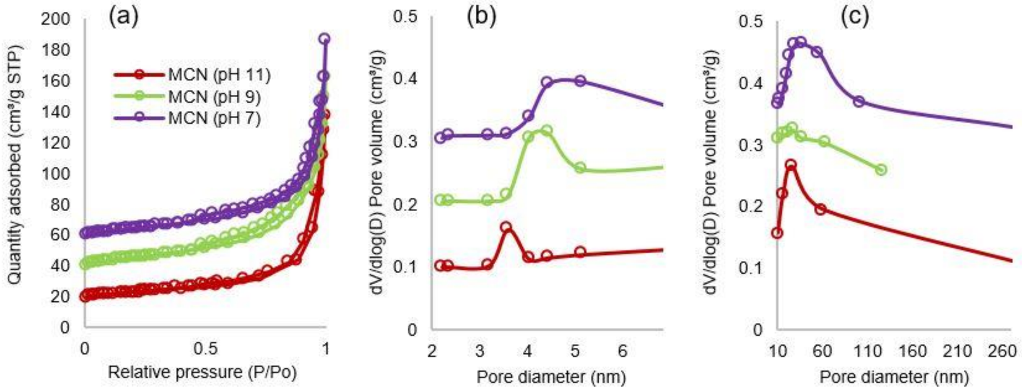

Figure 2: N_2 adsorption-desorption graphical data for MCN adsorbents at pH 7, 9 and 11; (a) N2 adsorption-desorption isotherm for all samples, (b) pore size distribution range of 2-7 nm, (c) pore size distribution range of 10-210 nm.

All samples showed a bimodal pore structure consisting of framework mesopores at 3–5 nm and textural mesopores at 60–260 nm. The MCN (pH 7) and MCN (pH 9) had same narrow distribution which was around 4 nm while the MCN (pH 11) was around 3.5 nm in the pore diameter range of 2-7 nm. In the pore diameter range of 10-260 nm, broad distributions were observed for MCN (pH 7) and MCN (pH 11) at the range of 26 nm to 56 nm. The distributions indicate large pore size and narrow pore size distribution centered around ~30 nm ~60 nm (Li et al., 2010). The different in pH value for MCN has influenced the mesopore distribution of all samples.

3.3 Effect of surfactant molar ratios and preparation method of MCN

As shown in Table 3, an inclining trend of surface area was observed with the increase of the Ceria/Surfactant ratio. MCN-2S (sol gel method) had the biggest surface area of 76.0 $m^2 g^{-1}$ and smallest pore diameter of 5.3 nm. Noticeably, numbers of pores increase as the surface area increases. However, the results of pore volume and pore diameter showed inconsistencies upon different Ceria/Surfactant ratio may have been affected during adsorbent preparation such as temperature, stirring and mixing effect. There was a sudden reduction in pore volume of MCN-2S which was 0.100 $cm^3 g^{-1}$ and MCN-2H (hydrothermal method) pore diameter increased slightly to 8.9 nm. These results demonstrate the smaller the pore size led to the greater the surface area of the adsorbent. Lower pore volume of MCN-2S may be attributed to the pore blockage from higher Ceria/Surfactant ratio. In addition, MCN-2S was chosen as the best adsorbent and best preparation method because it possessed high BET surface area, average pore volume and small pore diameter.

Table 3: Textural properties for commercial CeO_2 and MCNs with different surfactant to ceria ratio and preparation methods (sol gel and hydrothermal)

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
CeO_2	8.7	0.031	13.1
MCN-0.5H	56.3	0.111	7.9
MCN-1H	59.0	0.110	7.4
MCN-1.5H	68.6	0.139	8.2
MCN-2H	72.5	0.162	8.9
MCN-2S	76.0	0.100	5.3

Although the isotherms in Figure 3a correspond to a type IV curves as well as H1 hysteresis loops (Qu et al., 2014), MCN-2S still displayed a uniform cylindrical pores distribution and highly mesoporous structure. The MCN-2S had the highest steepness compared to CeO_2 and MCN-2H. An increased in adsorption uptake was observed in the high partial pressure region (P/P_0) around 0.5 to 1.0 for all samples. MCN-2H exhibited larger N_2 uptake compared to MCN-2S from (P/P_0) 0.8 to 1.0, which reflects the presence of mesopores. Meanwhile N_2 uptake of MCN from P/Po more than 0.2 was smaller compared to MCN-2S indicates MCN had less mesopores. MCN-2S had smaller N_2 uptake due to some of mesoporous were lost after calcination at higher temperature. MCN-2S (sol gel method) in Figure 3b had the highest distribution centred at 5 nm. A narrow distribution was observed at 18 nm and no distribution shown from the commercial CeO_2. Meanwhile in Figure 3c, MCN-2H exhibited small distribution around 20 nm. This indicates that concentration pore around 5 nm at small region of pore diameter was bigger than hydrothermal method. Whereas the MCN had no respond in the graph which indicates no presence of mesopores in the sample.

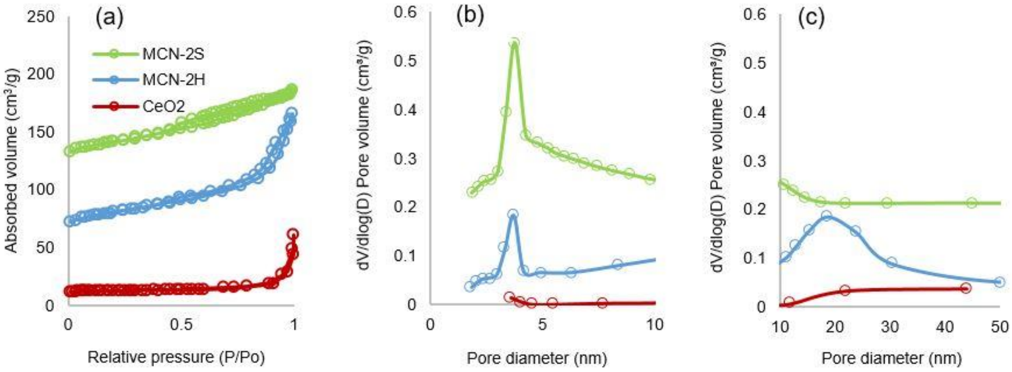

Figure 3: N_2 adsorption-desorption graph for CeO_2 and MCNs at different preparation methods; (a) N_2 adsorption-desorption isotherm of all samples, (b) pore diameter range from 0-10 nm MCN, and (c) pore diameter range from 10-50 nm for MCN.

3.4 CO2 capture performance and stability test

Figure 4a recaps the CO_2 uptake readings on both MCN-2S and MCN-2H. MCN-2S had bigger CO_2 uptake of 213.8 μmol g^{-1} while MCN-2H showed a significant amount of CO_2 uptake about 203.9 μmol g^{-1}. The higher uptake capacity of MCN-2S can be related to difference in surface area (76.0 m^2 g^{-1}) compared to MCN-2H surface area (72.5 m^2 g^{-1}) as shown in Table 3. Improved adsorption capacities of MCN-2S may be associated to higher diffusion rate of CO_2 through the mesoporous structure of the adsorbent (Ojeda et al., 2017). This fact was supported with a high pore volume of MCN-2S (0.100 cm^3 g^{-1}) able to facilitate the diffusion and contact between CO_2 and the surface of the adsorbent.

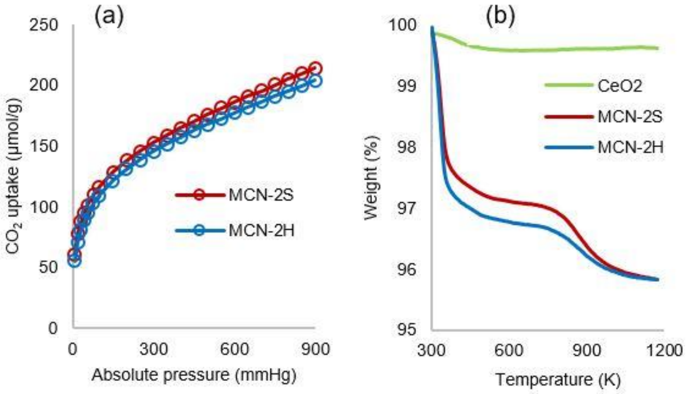

Figure 4: (a) CO_2 uptake readings on various sample of preparation method on MCN, (b) Thermal gravimetric analysis on various samples of MCN.

Previous study reported the CO_2 uptake for mesoporous CeO_2 achievable up until 132 μmol g^{-1} (Yoshikawa et al., 2014) which is lower compared to the studied MCN-2H and MCN-2S. Together with study done by Guo et al (2016) has reported that zirconium (Zr) doped calcium oxide (CaO) based adsorbent were synthesized via simple sol gel method and produced high CO_2 uptake capacity (0.64 g CO_2 g^{-1}sorbent) with favorable stability. The thermogravimetric measurements in Figure 4b shows the decomposition of adsorbent begins at 333 K and ends at 1172 K. Both MCN-2S and MCN-2H had equal weight loss, 6.885% compared to commercial CeO_2 which is around 0.400%. The obvious weight loss occurred between 373 K-423 K and 570 K-960 K was due to the releasing of adsorbed water and loss of residual additives. This proves that the MCN had an excellent thermal stability because it can withstand up until 1,173 K and experienced weight loss merely 7%.

4. Conclusion

This study presents a sol-gel and hydrothermal method being used to synthesize MCNs and were successfully characterized by N_2 adsorption-desorption isotherms and TGA method. The best parameters from this study were obtained via sol gel method at pH 9, calcination temperature of 673 K and Ceria/Surfactant ratio of 2. The MCN prepared by sol gel method showed high surface area of 76.0 $m^2 g^{-1}$ compared to hydrothermal method. The MCN showed high CO_2 uptake of 213.8 μmol g^{-1} with an excellent thermal stability up until 1173 K. In addition, sol-gel method has shown a cost effective in which the prepataion was done at room temperature instead of at high temperature comparing to hydrothermal method. Furthermore, sol-gel method showed better results in terms of overall textural properties, pore size distribution, CO_2 uptake and thermal stability compared to hydrothermal method. Further improvements on MCN can be made in order to improve the adsorption performance by various modifications. This type of adsorbent could be a potential to be used in industrial adsorption process in curbing the industrial flue gas emission.

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