Development of Mesoporous Magnesium Oxide-Alumina Composites for CO₂ Capture

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Abstract

Mesoporous magnesium oxide-alumina composites were synthesized by evaporation induced self assembly (EISA) in the presence of triblock copolymer Pluronic P123 in absolute ethanol solution. These mesostructures were prepared using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as alumina and MgO precursors, respectively. Block copolymer was completely removed by thermal treatment of as-synthesized samples at 350 °C in flowing nitrogen. Thermally treated composites displayed relatively high specific surface area and large pore volume. Temperature programmed desorption (TPD) was used to investigate the active sites available on the surface of the aforementioned samples for CO₂ sorption at 120 °C. Magnesium oxide-alumina composite samples showed an enhanced CO₂ uptake under flue gas conditions (100~150 °C). The sample synthesized from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ only showed adsorption capacity of about 1.30 mmol/g. Incorporation of 10 molar % of MgO did not significantly increase the CO₂ uptake of the alumina-based composite; however, incorporation of 30 molar % of MgO increased CO₂ uptake up to 2.08 mmol/g. An increase of the MgO content in the composite caused a gradual enhancement in the CO₂ uptake; namely, the composite with 70 % of MgO loading showed 2.87 mmol/g CO₂ uptake. High thermal and mechanical stability of the composites studied as well as their low cost, good resistance to the corrosion and oxidizing environment make these materials, especially MgO-rich composites, attractive candidates for CO₂ capture at flue gas conditions.

Keywords: Magnesium oxide-alumina composites, temperature programmed desorption, High temperature CO₂ capture.

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1.Introduction

Nowadays, global warming and climate changes are the key environmental concerns. A rapid increase in the world energy demand results in producing a vast amount of carbon dioxide every year by industry, especially by power plants and gas processing units. The total anthropogenic greenhouse gas emissions, which mainly come from fossil fuels, will probably rise from 26 Gt in 2004 to 37-40 Gt or more in 2030 [1]. Such greenhouse gas emissions can cause a 2- 4 °C rise in temperature during the next century, if atmospheric levels of heat trapping gases such as CO₂, SO₂, NO, N₂O, NO₂, and CH₄ are not reduced. Significant fluctuation in this temperature can possibly produce unforeseen weather events, such as droughts and floods. Even a small change in temperature can be sufficient for melting glaciers and rising sea level, which may result in destroying natural ecosystems and reducing biological diversity. Thus, the reduction of atmospheric CO₂ concentration is of great importance to maintain global climate. This reduction can be achieved by various ways, for instance, by employing high capacity sorbents for CO₂ capture.

At present, CO₂ is often captured by using aqueous amine-based processes, but this technology has several drawbacks such as high cost due to the degradation of amines and corrosive environment. There is a great challenge to prepare sorbents for CO₂ capture at flue gas conditions (100~150 °C) because at high temperatures the CO₂ sorption capacity is low. Also, the impurities present in flue gases such as nitrogen and sulfur oxides often reduce the efficiency of the sorbents used [1]. Thus, there is a strong demand from industry to develop effective and low cost sorbents for CO₂ capture at elevated temperatures.

Modification of thermally stable porous solids by incorporating basic species is essential for enhancing interactions with acidic CO₂ to increase CO₂ sorption capacity and selectivity. Among

various solids, oxides of alkaline metals (Na, K) [2,3], alkaline earth metals (Ca, Mg) [2,4,5], transition metals (Zr, Ni) [6,7], and aluminum (Al) [8,9] have been often used for the development of sorbents for CO₂ capture. For instance, different MgO, MgO-MCM-41, MgO/Al₂O₃, and MgO-ZrO₂ composites have been extensively studied for CO₂ sorption at different temperatures (0-150 °C) [4,10]. A lithium-containing sorbent was also tested for CO₂ capture by Nakagawa and co-workers [11]. Interaction of carbon dioxide with the surface of zirconia polymorphs was also investigated by several groups [6,12,13]. Recently, Ni-containing catalysts incorporated into ordered mesoporous MgO-Al₂O₃ composites were explored for CO₂ reforming of CH₄ [14]. These catalysts exhibited high activity and long term stability toward CO₂ reforming of CH₄. Note that MgO basic sites have greatly enhanced chemisorption and activation of CO₂ that consequently resulted in better catalytic activity and stability of the aforementioned catalysts. Among various oxides, the alumina-based composites containing MgO are worthy to explore because they possess basic sites and show high thermal and mechanical stability. These properties are crucial for the development of effective sorbents for CO₂ capture at elevated temperatures, which in addition should be inexpensive and possess high CO₂ sorption capacity, good selectivity in the presence of impurities, and favorable sorption kinetics [1].

This work reports the synthesis of MgO-Al₂O₃ composites with well-developed porosity, high surface area, and enhanced basic properties by employing block copolymer-assisted evaporation induced self-assembly (EISA) sol-gel synthesis under acidic conditions[15]. Although alumina possesses some basic sites, magnesium oxide was further incorporated during one-pot sol-gel synthesis to increase the basicity of the resulting porous composites and to improve their thermal stability, which is desirable during CO₂ capture at elevated temperatures, 100~150 °C. The CO₂sorption capacity of the composites studied at elevated temperature (120 °C) was

investigated by temperature programmed desorption (TPD).

2. Materials and methods

Triblock copolymer Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was donated by BASF Corporation, Florham Park, New Jersey. Absolute ethanol was obtained from Aaper Alcohol and Chemical Co., Shelbyville, Kentucky. 95 % Ethanol was purchased from Fisher Scientific, Pittsburgh, Pennsylvania. Aluminum nitrate nanohydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and magnesium nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sigma Aldrich. All reagents were analytical grade and used without further purification.

Mesoporous alumina-based composites with incorporated MgO and ZrO_2 were synthesized using a slightly modified recipe reported by Cai et al. [15]. In this synthesis, 1.0 g of Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and the specified amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to 30 mL of absolute ethanol in a 250 mL polypropylene wide mouth bottle. The resulting mixture was stirred at room temperature for 70 min. Next, the specified amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added. The resultant mixture was stirred at room temperature for additional 4 hours. The final solution was kept in an oven at 60 °C for 48 hours. The product was heated in a horizontal quartz tube furnace at 400 °C for 2 hours in flowing N_2 with heating rate of 3 °C/min.

The resulting samples were labeled as AMX where A and M refer to alumina and MgO, respectively, and X denotes the molar percentage of MgO in the composite sample. The as-prepared, extracted, and calcined (extracted followed by thermal treatment in nitrogen at 400 °C) samples are differentiated by adding a, e and c, respectively. The molar percentage of MgO was calculated as follows: $X \% = [\text{Mg moles} \times 100] / [\text{Mg moles} + \text{Al moles}]$. The number of Al moles was kept constant (0.01 mol) during the synthesis. Acnotation refers to the thermally

treated sample synthesized in the presence of Pluronic P123 from aluminum nitrite only. Similarly AM10c refers to the thermally treated sample synthesized using 10% of magnesium nitrite and 90% of aluminum nitrate.

3.Characterization

3.1 Measurements

Nitrogen adsorption isotherms were measured at -196 °C on ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA). Prior to the adsorption measurements, all samples were outgassed under vacuum at 110 °C for 2 hours.

High resolution thermogravimetric measurements were recorded on TGA Q-500 analyzer (TA Instruments, Inc., New Castle, DE). Thermogravimetric (TG) profiles were recorded from 25 °C up to 700 °C in flowing nitrogen with a heating rate of 10 °C / min using a high resolution mode. The weight of each analyzed sample was typically in 5-20 mg range. The TG profiles were used to obtain information about the extent of template removal.

3.2 CO₂ Physisorption Measurements

CO₂ adsorption on the AMX composite samples was measured in the pressure range up to 1 atm on ASAP 2020 (Micromeritics, Inc., GA) volumetric adsorption analyzer at 25 °C using ultrahigh purity (99.99 %) CO₂. Prior to analysis, samples were outgassed at 110 °C for 2 h under vacuum

3.3 CO₂ Chemisorption-TPD Measurements

To evaluate the CO₂ sorption on the calcined samples, the temperature-programmed desorption (TPD) experiments were conducted using a Micromeritics Auto Chem II Chemisorption

Analyzer (Norcross, GA) equipped with a thermocouple detector (TCD). Approximately 50-100 mg of each sample were loaded in a quartz tube microreactor supported by quartz wool and subjected to pretreatment at 800 °C for 10 min before CO₂ sorption, using a heating rate of 10 °C/min in flowing helium (at 50 cm³/min). Next, the samples were cooled to selected temperature (120 °C) using heating rate of 10 °C/min and exposed to pulse of 5 % CO₂-He (50 cm³/min). In the TPD experiments, the samples were heated up to 800 °C using a heating rate of 5 °C/min and kept at this temperature for 90 min. The amount of desorbed CO₂ was obtained by integration of the desorption profiles and referenced to the TCD signals calibrated for the known volumes of analyzed gases.

3.4 Calculations

The Brunauer-Emmett-Teller specific surface area (S_{BET}) for the samples studied was calculated from N₂ adsorption isotherms in the relative pressure range of 0.05-0.20. The single-point pore volume (V_{sp}) was estimated from the amount adsorbed at a relative pressure of ~ 0.98. The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by the improved KJS method calibrated for cylindrical pores [16]. The pore width (W_{max}) was obtained at the maximum of the PSD curve.

4. Results and discussion

4.1 Properties of MgO-Al₂O₃ composite samples

Thermal degradation of as-synthesized, extracted, and thermally treated (calcined) MgO-Al₂O₃ materials in flowing N₂ are displayed in Figure 1. The TG and DTG profiles for the representative as-synthesized AMX materials are compared to those of the extracted and calcined samples. The DTG profiles obtained for the AM10a samples exhibit three peaks at the

temperature ranges from 90-120 °C, 200-300 °C, and 300-500 °C due to evaporation of physically adsorbed water and possibly solvent, thermodesorption/degradation of P123 block copolymer template, and dehydroxylation of OH groups, respectively. Figure 1 further demonstrates that the extraction alone is not effective to remove the entire amount of the block copolymer template; thus, an additional controlled calcination was used to remove the aforementioned block copolymer from the as-synthesized mesostructures. The TG curves obtained for calcined samples show a weight loss step at around 500 °C, which is possibly due to the condensation of surface hydroxyl groups.

Figure 1: TG and DTG profiles for the as-synthesized (a), extracted (e), and calcined (c) MgO- Al_2O_3 samples.

Table 1 shows the specific surface area and pore volume values for thermally treated MgO- Al_2O_3 composites, which are relatively high. Nitrogen adsorption isotherms and the corresponding

PSD for the composite samples studied are shown in Figure 2. All isotherms are type IV with H1 type hysteresis loops in the range of 0.5-0.8 relative pressure. The BET surface areas for the series of AMXc samples ($X = 10, 30, 50, 70$) are in the range of 200-300 m^2/g and the single point pore volume (V_{sp}) varies from 0.40 to 0.45 $\text{cm}^3 \text{g}^{-1}$ (Table 1 & Figure 2). The pore size distributions calculated by the KJS method are quite narrow for AM50c and AM70c, whereas those for AM10c and AM30c are bimodal. The pore diameters obtained at the maximum of the PSD curves for AMXc ($X = 10, 30, 50, 70$) samples are in the range of 5.4-12.7 nm and decrease with increasing MgO content in the MgO- Al_2O_3 composites.

Figure 2. Nitrogen adsorption-desorption isotherms (left panel) and the corresponding PSD curves (right panel) for AMXc samples (all isotherms and PSD curves are shifted by multiple of 200 $\text{cm}^3 \text{STP/g}$ and 0.05 cm^3/g , respectively).

Table 1. Adsorption parameters for the samples studied.

sample	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{sp} (cm^3/g)	W_{max} (nm)
AM10c	275	0.04	0.43	12.7
AM30c	290	0.04	0.41	9.2
AM50c	223	0.02	0.40	9.9
AM70c	283	0.02	0.45	5.4

S_{BET} -specific surface area calculated from adsorption data in relative pressure range of 0.05-0.20; V_{sp} - single point pore volume calculated at the relative pressure of 0.98; V_{mi} - volume of fine pores (micropores and small mesopores below 3 nm) calculated by integration of the PSD curve up to 3 nm; W_{max} - pore width calculated at the maximum of PSD, using improved KJS method.

4.2 CO₂ chemisorption

The MgO-Al₂O₃ composite samples were subjected to pretreatment in flowing He in TPD analyzer followed by preferential pulse CO₂ chemisorption at 120 °C and subsequent desorption by ramping temperature up to 800 °C. As can be seen from Figure 3, after thermal pretreatment of the sample, a steady stream (pulse chemisorption) of CO₂ flows through the sample and is sorbed on the available active sites. The most of chemisorbed CO₂ on the AMXc(X = 10, 30, 50, 70) samples at 120 °C was desorbed at 507 °C(Figure 4).

Figure 3. Pretreated, pulse, and CO₂ TPD profiles measured for AM50c sample

Figure 4. CO₂ TPD (pulse at 120 °C) profiles recorded for the MgO-Al₂O₃ samples studied.

As can be seen from Figure 4 showing the TPD profiles, the CO₂ sorption capacity increases with increasing MgO content in the composites. A small amount of MgO (10%) in the composite did not enhance significantly the CO₂ uptake. However, 30 % of MgO in the composite sample increased the CO₂ uptake substantially. The CO₂ sorption data for the samples studied show a gradual decrease in the CO₂ uptake in the following order: AM70c > AM50c > AM30c > AM10c. The highest CO₂ uptake of 2.87 mmol/g at 120 °C was obtained for the composite sample with highest MgO content, AM70c. The amounts of thermodesorbed CO₂ listed in Table 2 are competitive in comparison to the values reported in literature.

Table 2. CO₂ uptake at 120 °C for the samples studied.

sample	CO ₂ uptake (mmol/g)
AM10c	1.47
AM30c	2.08
AM50c	2.46
AM70c	2.87

The amounts of desorbed CO₂ was obtained by integration of the TPD profiles.

For instance, the CO₂ sorption capacities reported for mesoporous alumina and alumina-supported metal oxides (Ca, Mg, Ce, Cu, Cr) at 120 °C by Cai and co-workers [15] did not exceed the value of 1.8 mmol/g. The CO₂ uptakes measured on a zeolite at 120 °C by Siriwardena and co-workers achieved the values of 0.7 and 1.2 mmol/g at 1 and 20 bar, respectively [17]. The CO₂ capacities measured on a MgO-Al₂O₃ composite sorbent at 60 °C were equal to 0.97 and 1.36 mmol/g in the presence (13%) and absence (0%) of water vapor, respectively [18]. The highest value of CO₂ uptake obtained from mesoporous isocyanurate-containing organosilica-alumina composites at 120 °C was of about 2.2 mmol/g [19].

Figure 5. EDX spectrum obtained for the AM50c sample.

The highest CO₂ uptake of 2.87 mmol/g recorded for AM70c in this work was possible due to the incorporation of basic oxide MgO into mesoporous alumina. The powder XRD analysis was performed to check the crystallinity of the MgO-Al₂O₃ samples studied. As expected this analysis showed that the samples are amorphous because their thermal treatment was carried out at relatively low temperature, 400 °C [19]. However, the presence of Mg and Al in the composite

oxides was confirmed by the EDX analysis (see Figure 5), indicating that the added $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ have been transformed to respective oxides.

4.3 CO₂ physisorption

MgO-Al₂O₃ mesostructures were also examined for CO₂ adsorption at room temperature (25 °C). Equilibrium CO₂ adsorption isotherms for the composite samples studied are shown in Figure 6, while Table 3 contains the corresponding CO₂ uptakes at 1 bar. As can be seen from Table 3 the incorporation of MgO into mesoporous alumina did not cause a significant change in the CO₂ uptake at 25 °C as compared to the chemisorption values at 120 °C. The structural parameters of the composite samples such as the specific surface area and the volume of ultramicropores (pores below 1 nm [20]) determine the CO₂ adsorption at ambient conditions, while basic sites are essential for chemisorption.

Table 3. Structural parameters and CO₂ uptake at 25 °C for the samples studied^a.

Samples	S_{BET} (m ² /g)	V_{mi} (cm ³ /g)	Maximum CO ₂ adsorption n_{CO_2} (mmol/g)	Max CO ₂ adsorption (μmol/m ²) $n^* \text{CO}_2$
AM10c	275	0.04	1.75	6.4
AM30c	290	0.04	1.82	6.3
AM50c	223	0.02	1.36	6.1
AM70c	283	0.02	1.41	5.0

^a S_{BET} -specific surface area calculated from adsorption data in relative pressure range of 0.05-0.20; V_{mi} - volume of fine pores (micropores and small mesopores below 3 nm) calculated by integration of the PSD curve up to 3 nm; n_{CO_2} -number of moles of CO₂ adsorbed per gram of the sample; $n^* \text{CO}_2$ -number of moles of CO₂ adsorbed per unit surface area of sample.

Figure 6. CO₂ adsorption isotherms at 25 °C measured for the MgO-Al₂O₃ samples studied.

As can be seen from Table 3 even a small increase in the volume of fine micropores has a pronounced effect on the CO₂ uptake recorded for the AMXc (X=10, 30, 50, and 70) samples at ambient temperature. For instance, the CO₂ uptake increased from 1.41 mmol/g for AM70c to 1.75 mmol/g for AM10c at 25 °C (see Figure 5 and Table 3). Although AM30c showed the same volume of micropores as the AM10c sample, the CO₂ sorption capacity recorded for AM30c was 1.82 mmol/g, which is slightly higher than that recorded for AM10c (1.75 mmol/g). This small increase can be due to the slightly higher surface area of AM30c (290 m²/g) in comparison to that of AM10c (275 m²/g) (see Table 1). Although the surface area and pore volume of the composite samples studied are, respectively, in the range of 220-290 m²/g and 0.40-0.45 cm³/g (Table 1), their microporosity is small (0.02-0.04 cm³/g), which is not surprising for alumina-based materials. Note that the CO₂ uptake values recorded at 25 °C and 1 bar for the series of samples studied do not exceed 2 mmol/g as compared to the corresponding values obtained at 120 °C, which approach 3 mmol/g for the samples with MgO loading of 30% or higher (see Table 1).

Conclusions

A series of MgO-Al₂O₃ was prepared and examined for CO₂ sorption at 25 °C and 120 °C; these materials exhibit high values of the CO₂ sorption capacity in the range of 1.47 to 2.87 mmol/g at 120 °C. Thus, the materials studied appear to be attractive for CO₂ capture in fossil fuel-based power plants, which produce large volumes of gases with low partial pressure of CO₂ at the temperatures range of 100 - 150 °C. The CO₂ adsorption isotherms measured at 25 °C for these materials show lower CO₂ uptakes than those obtained at 120 °C because the volume of micropores, which determines CO₂ adsorption at ambient conditions, is in the range of 0.02-0.04 cm³/g. Importantly, the aforementioned materials are thermally stable and resistant to oxidative degradation in an inert atmosphere. Further improvement of the specific surface area, microporosity, and chemical composition of the aforementioned composites is possible to enhance their potential for CO₂ capture at elevated temperatures.

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References

- [1] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar and R. Gupta, Ind. Eng. Chem. Res., 51(2012)1438-1463.
- [2] R.V. Siriwardena, C. Robinson, M. Shen and T. Simonyi, Energy & Fuels, 21(2007) 2088-2097.
- [3] H. Hayashi, J. Taniuchi, N. Furuyashiki, S. Sugiyama, S. Hirano, N. Shigemoto and T. Nonaka, Ind. Eng. Chem. Res., 37(1998) 185-191.

- [4] L. Li, X.Wen, X. Fu, F.Wang, N. Zhao, F. Xiao, W. Wei and Y. Sun, *Energy & Fuels*, 24 (2010) 5773-5780.
- [5] A.Zukal, J. Pastva and J. Cejka, *J.Microporous and Mesoporous Mat.*, 167(2013) 44-50.
- [6] V.Hornebecq, C. Knofel, P. Boulet, B. Kuchta and P.L. Llewellyn, *J. Phys. Chem. C*, 115 (2011) 10097-10103.
- [7] J.Liu, Y.Wang, A.I. Benin, P. Jakubczak, R.R.Willis and M.D.Levan, *Langmuir*, 26(2010) 14301-14307.
- [8] Z.Yong, V.Mata and A.Rodrigues, *J.Chem.Eng.Data*, 45 (2000) 1093-1095.
- [9] W.Chaikittisilp, J.K. Hyung and C.W.Jones, *Energy and Fuels*, 25(2011), 5528-5537.
- [10] S.J. Han, Y. Bang, H. Lee, K. Lee, I.K. Song, J.G. Seo, *Chem. Eng. J.*, 270(2015) 411-417.
- [11] M. Kato, S.Yoshikawa and K. Nakagawa, *J. Mater. Sci. Lett.*, 21 (2002) 485-487.
- [12] B.B. Baeza, I.R. Ramos and A.G. Ruiz, *Langmuir*, 14 (1998) 3556-3564.
- [13] K. Pokrovski, K.T. Jung and A.T. Bell, *Langmuir*, 17(2001) 4297-4303.
- [14] L.Xu, H. Song, L. Chou, *Int. J. Hydrogen. Energ.*, 38(2013) 7307-7325.
- [15] W.Cai, J. Yu, C.Anand, A.Vinu and M.Jaroniec, *J.Mater.Chem*, 23 (2011) 1147-1157.
- [16] M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 13 (1997) 6267-6273.
- [17] R.V.Siriwardena, M.S.Shen and E.P.Fisher, *Energy & Fuels*, 19 (2005) 1153-1159.
- [19] C. Gunathilake, M. Gangoda and M. Jaroniec, *J. Mater. Chem. A*, 1(2013) 8244-8252.
- [20] N.P. Wickramaratne and M. Jaroniec, *J. Mater. Chem. A*, 1(2013) 112-116.

Graphical Abstract