

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 Al(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O 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 Al(NO₃)₃·9H₂O 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.

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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 Kato et al.

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[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 CO₂ sorption 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 (EO₂₀PO₇₀EO₂₀) 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 Al(NO₃)₃·9H₂O and magnesium nitrate hexahydrate Mg(NO₃)₂·6H₂O were purchased from Sigma–Aldrich. All reagents were analytical grade and used without further purification.

Mesoporous alumina-based composites with incorporated MgO and ZrO₂ were synthesized using a slightly modified recipe reported by Cai et al. [15]. In this synthesis, 1.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) and the specified amount of Al(NO₃)₃·9H₂O 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 Mg(NO₃)₂·6H₂O was added. The resultant mixture was stirred at room temperature for additional 4 h. The final solution was kept in an oven at 60 °C for 48 h. The product was heated in a horizontal quartz tube furnace at 400 °C for 2 h in flowing N₂ 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. Ac notation 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 h.

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 upto 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

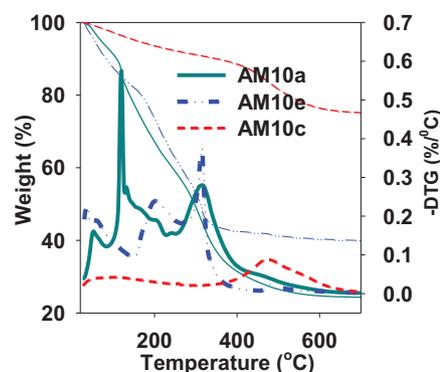


Fig. 1. TG and DTG profiles for the as-synthesized (a), extracted (e), and calcined (c) MgO–Al₂O₃ samples.

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