Carbon dioxide adsorption on mesoporous magnesium carbonate

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Abstract

Mesoporous magnesium carbonate (MMC) was synthesized and tested for its ability to separate CO₂ from N₂. The pure gas CO₂ uptake of MMC was around 1.5 mmol/g at 101 kPa, 0 °C. The N₂ uptake under the same conditions was less than 0.1 mmol/g. Al(NO₃)₃, Al₂O₃, K₂CO₃ and KNO₃ were introduced into the porous structure of MMC as additives. All of the additives tested increased the CO₂ uptake of MMC and increased its selectivity towards CO₂. The incorporation of 5 wt.% K₂CO₃ increased the CO₂ uptake of MMC up to over 3.2 mmol/g. The ideally adsorbed solution theory was used to calculate the CO₂ selectivity of MMC and MMC with additives for a hypothetical gas mixture that contained 15% CO₂: 85% N₂. The CO₂ selectivity at 101 kPa (0 °C) was around 60. MMC with 5 wt.% K₂CO₃ had a CO₂ selectivity of over 150 under the same conditions. Vacuum swing cyclic CO₂ adsorption/desorption showed that the CO₂ uptake on MMC with 5 wt.% K₂CO₃ decreased after each cycle. Heat regeneration (up to 250 °C, for 10 minutes) could recover most of the lost CO₂ capacity after each cycle. Heat regeneration indicatively improved the cyclic performance of this adsorbent. MMC with 5 wt.% K₂CO₃ was the best performing adsorbent in this study and can potentially be further developed into a good CO₂ adsorbent for temperature swing adsorption (TSA) processes.

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Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: Carbon Capture and Storage, Gas separation, Adsorbent, Magnesium carbonate

1. Introduction

Carbon dioxide, as a greenhouse gas and the product of fossil fuel combustion, is regarded as a pollutant and is emitted in large quantities due to human activities. The increasing levels of atmospheric CO₂ is considered to be...
related to global warming due to the greenhouse effect. There is an urgent need to bring the amount of CO₂ emission under control. Scientist and engineers are continuously working on methods to reduce the emission of CO₂. One method could be to tackle CO₂ emission from point sources, such as a coal burning power plant. The exhaust gas from a coal burning power plant (referred to as “flue gas”) typically contains around 15 vol.% of CO₂ in a mixture of N₂. Other gases, such as SO₂, O₂ and H₂O can also be present in minor amounts. [1, 2] One idea to reduce the CO₂ emission is to remove CO₂ from flue gas before it is released into the atmosphere. Currently, amine based absorption processes are implemented for the removal of CO₂ from flue gas. Newly emerged technologies, such as adsorption based CO₂ capture, has received an increased level of attention in recent years due to the potentially low operating costs. [3] Adsorption based CO₂ capture technologies include pressure/vacuum, or temperature swing adsorption (P/VSA or TSA). In each case, the choice of adsorbent is vital for the overall performance of the CO₂ capture process. For CO₂ capture from a stream of cooled flue gas at ambient temperature, a low cost adsorbent with high CO₂ capacity, high CO₂ selectivity, and a long cyclic lifetime would be desirable. [4] Many types of materials, including zeolites, [4] metal organic frameworks, [3, 5] porous carbons [6] and silicates [7] have been well studied as potential CO₂ adsorbents for CO₂ capture from flue gas.

Here, we studied mesoporous magnesium carbonate (MMC) as an adsorbent for CO₂ capture from flue gas. MMC is a highly porous, X-ray amorphous magnesium carbonate material first reported in 2013. [8] MMC is synthesized using MgO and CO₂ as starting materials in a methanol solvent. No additives or surfactants are required and the synthesis itself can be easily upscaled. The average pore size of the mesopores on MMC can be adjusted from around 2 – 20 nm by adjusting the drying conditions. [9] We have previously demonstrated the functionality of the mesopores of MMC.[10-12] The effect of several additives on the CO₂ adsorption properties of MMC was also investigated here.

2. Experimental

2.1. Synthesis of MMC

The synthesis of MMC is documented elsewhere. [9] In summary, 20g of MgO was homogeneously dispersed in 300 ml methanol by stirring in a reinforced glass reaction vessel purchased from Andrew Glass Co., USA. The mixture was then pressurized with 4 bar of CO₂ and sealed for 24 h at room temperature under stirring. Gelation of the clear colloidal suspension obtained after 24 h was induced by heating and the gel was dried into powder form by heating to 150 °C for 3 hours.

The synthesis of MMC with additives was carried out in a similar manner as described above. Different amounts of additives (Al(NO₃)₃, Al₂O₃, KNO₃ and K₂CO₃) were added to the colloidal suspension before drying. The suspension was then gently heated under stirring until it turned into a thick gel. The gel was then dried into a powder at 150 °C until it was completely dry.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced XRD Twin-Twin instrument (45 kV and 40 mA) with Cu-Kα radiation (λ=1.5418 Å) in the 2Ɵ range from 10° to 90°. Scanning electron microscopy (SEM) images were recorded using a Zeiss LEO 1530 scanning electron microscope operating at 2 kV.

N₂ adsorption/desorption at -196 °C, CO₂ and N₂ adsorption isotherms at 0 °C, were recorded using a Micromeritics ASAP2020 surface area analyzer. The samples were prepared at 100 °C under dynamic vacuum for a minimum of 6 hours prior to analysis.

The CO₂ selectivity of the adsorbents was modelled using the ideally adsorbed solution theory (IAST). The collected CO₂ adsorption isotherms were modelled using a two-site Langmuir isotherm equation and the N₂ isotherms were modelled using a single-site Langmuir isotherm equation. The IAST selectivity of each sample from a pressure range between 0 and 101 kPa was calculated using MatLab 2014b with a set of codes written by us. The hypothetical flue gas considered here contained 15 vol.% CO₂ and 85 vol.% N₂.
3. Results and Discussion

3.1. MMC characterization

The high specific surface area and porosity of the obtained MMC was characterized by the N₂ adsorption/desorption isotherm shown in Figure 1. The specific Brunauer–Emmett–Teller (BET) surface area of MMC was around 640 m²/g and the total pore volume was around 0.54 cm³/g. The average pore size of the mesopores on MMC obtained for this study was around 3.8 nm, some micropores (<2 nm in diameter) were also detected on the sample. We previously showed that MMC is made up of nanoparticles of several nm in size that aggregate together forming agglomerates, with the porosity of the material being the space between these nanoparticles. Furthermore, the small size of these nanoparticles also meant that MMC was X-ray amorphous, as shown in the powder XRD pattern in Figure 1 (right). The SEM images shown in Figure 2 confirmed the presence of nanoparticles that have been aggregated together to form MMC. (Note that the size of the nanoparticles shown in the image is not representative due to sample coating with a layer of gold/palladium nanoparticles)

![Figure 1. N₂ adsorption/desorption of MMC (left), powder XRD pattern of MMC (right)](image)

3.2. CO₂ adsorption on MMC

The CO₂ and N₂ adsorption isotherms (at 0 °C) of MMC are shown in Figure 3 (left). CO₂ was preferably adsorbed over N₂ across the entire tested pressure range. The CO₂ uptake of MMC reached over 1.51 mmol/g at 101 kPa (0 °C). In contrast, the CO₂ uptake at 101 kPa (at 0 °C) on purchased MgCO₃ (basic MgCO₃, purchase from SigmaAldrich) and MgO (high purity, purchased from SigmaAldrich) were 0.19 and 0.46 mmol/g, respectively (Figure 3, right). MMC showed significantly higher CO₂ uptake than purchased MgCO₃ and MgO across the entire pressure range tested. The high CO₂ uptake on MMC was mainly related to its high specific surface area and porosity, which allowed CO₂ physisorption to take place extensively.

![Figure 2. SEM images of MMC at different magnification](image)
3.3. CO₂ adsorption on MMC with additives

In order to further improve the performance of MMC as an adsorbent, a selection of different additives (Al(NO₃)₃, Al₂O₃, K₂CO₃ and KNO₃) were incorporated into MMC. The Al based additives were chosen due to the strong affinity for CO₂ adsorption on Al in other material such as alumina,[13] and in order to mimic the chemical compositions of a type of well-studied Mg/Al based CO₂ adsorbent - hydrotalcite. The K based additives were chosen as they have previously shown promising effect on increasing the CO₂ uptake on hydrotalcites at moderate temperature.[14] The composition of these samples and their BET specific surface area are listed in Table 1 together with CO₂ uptake and selectivity data. For the K based additives 5 wt% and 10 wt% were tested to see the dosage dependence, 5 wt% performed the best for both of the additives and will therefore be discussed more in detail.

Table 1. The amount of additives on MMC and the BET surface area, CO₂ uptake and CO₂ selectivity of these samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Additive and amount</th>
<th>BET surface area</th>
<th>CO₂ uptake at 101 kPa</th>
<th>CO₂ selectivity</th>
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<td>MMC</td>
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<td>698</td>
<td>1.51</td>
<td>60</td>
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<tr>
<td>MMC-Al(NO₃)₃</td>
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<td>154</td>
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<tr>
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<td>2.49</td>
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<tr>
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<td>KNO₃, 10 wt.%</td>
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</table>

Figure 4. Powder XRD pattern of MMC with additives (left), SEM images of MMC-K₂CO₃ at different magnification (middle, right)

Powder XRD pattern of the MMC with additives (Figure 4 left) showed that MMC with additives remained amorphous, with minor diffraction peaks related to the additive itself seen for some samples. The overall structure of MMC was not changed as clearly seen from the SEM images of MMC with 5 wt.% of K₂CO₃ (MMC-K₂CO₃) (Figure 4, middle and right).
The CO$_2$ and N$_2$ adsorption isotherms of MMC with additives are displayed in Figure 5. All of the tested additives appeared to have positive effect on the CO$_2$ uptake. The CO$_2$ uptake of all MMC with additives increased, the uptake of N$_2$ under these conditions appeared to be unaffected by the additives. The effect being the most profound when 5 wt.% of K$_2$CO$_3$ was incorporated on MMC (for MMC-K$_2$CO$_3$). The CO$_2$ uptake of this sample increased to 3.21 mmol/g at 101 kPa (0 °C), over double of the CO$_2$ uptake of MMC under the same conditions.

The theoretical IAST CO$_2$ selectivity for a gas mixture containing 85% N$_2$ and 15 % CO$_2$ from 0 to 101 kPa was calculated for the different samples of MMC and shown in Figure 6 (left). At 0°C, the IAST selectivity reached over 60 at 101 kPa for MMC without any additives. The CO$_2$ selectivity was comparable with zeolite A.[4] (note that the extremely high selectivity at low total pressure is an artifact of the IAST model and should not be considered as realistic). The effect of additives on the CO$_2$ selectivity could also be seen, with the CO$_2$ selectivity of MMC-K$_2$CO$_3$ increased to over 150 at 101 kPa when compared with MMC. The CO$_2$ selectivity of MMC with different additives are listed in Table 1 for comparison. It was clear that the presence of additives could enhance both the CO$_2$ uptake and CO$_2$ selectivity of MMC. Out of the tested additives, 5 wt.% of K$_2$CO$_3$ had the largest effect on the CO$_2$ adsorption and separation ability of MMC.

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The cyclic performance of MMC-K$_2$CO$_3$ was tested with and without regeneration by heat treatment. Figure 6 (right) shows that without heat regeneration (recovery only by vacuum), the CO$_2$ uptake at 101 kPa (0 °C) decreased after each cycle. After 4 cycles, the CO$_2$ uptake at 101 kPa (0 °C) had decreased from 3.21 to 2.04 mmol/g. After the 4th cycle, heat regeneration was used instead of vacuum regeneration. Heat regeneration under a slow N$_2$ flow (~20 cm$^3$/min) at 150 °C for 10 minutes increased the CO$_2$ uptake of MMC-K$_2$CO$_3$ to 2.74 mmol/g for the 5th cycle. For the next cycle (cycle 6), the heat regeneration temperature was increased to 250 °C, which further increased the CO$_2$ uptake to 2.82 mmol/g (101 kPa, 0 °C). However, if the regeneration temperature was increased further to 300 °C (for cycle 7), the CO$_2$ capacity MMC-K$_2$CO$_3$ decreased to 1.99 mmol/g (101 kPa, 0 °C). These findings showed that CO$_2$ uptake on MMC-K$_2$CO$_3$ decreased with each cycle if regenerated by vacuum without heat, probably due to strongly physisorbed or chemisorbed CO$_2$. Heat regeneration under N$_2$ flow between 150 °C
and 250 °C could be used to improve the cycle performance of MMC-K₂CO₃. However, at temperatures above 250 °C irreversible structural changes occurred on MMC-K₂CO₃ and the CO₂ uptake capacity decreased as a result.

4. Conclusion

Mesoporous magnesium carbonate (MMC) with high porosity and BET surface area (over 600 m²/g) was synthesized and tested as potential CO₂ adsorbent in flue gas CO₂ separation. MMC has a good level of CO₂ uptake at 101 kPa (1.5 mmol/g) and high ideally adsorbed solution theory (IAST) selectivity towards CO₂ over N₂ (~60). The introduction of 5 – 10 wt.% of Al₂O₃, Al(NO₃)₃, K₂CO₃ and KNO₃ on to MMC improved the CO₂ adsorption of MMC. MMC containing 5 wt. % of K₂CO₃ as an additive adsorbed twice as much CO₂ under the same conditions (101 kPa, 0 °C) when compared with pure MMC. The IAST selectivity of this sample (MMC-K₂CO₃) also increased from 60 to over 150. Cyclic CO₂ adsorption experiments showed that the CO₂ capacity decreased with each cycle when vacuum is used as the method of adsorbent regeneration. Heat regeneration between 150 and 250 °C under N₂ flow for 10 minutes could be applied to MMC-K₂CO₃ to improve its cyclic performance. MMC-K₂CO₃ could be further developed as a CO₂ adsorbent in flue gas CO₂ capture using temperature swing adsorption (TSA) processes.

5. Reference