

## Catalytic Capture of CO<sub>2</sub> with Template-Containing Zn/MCM-41 and Its Transformation to Solid Carbonate

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Mesoporous MCM-41 materials modified by zinc have been prepared by non hydrothermal procedure. Zinc has been introduced by the direct synthesis (DS), template ion-exchange (TIE) and wet impregnation (WI) methods. The catalysts were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy-scanning electron microscopy (EDX-SEM), thermogravimetric and differential thermal analyses (TGA-DTA), Fourier transform infrared spectroscopy (FTIR) and N<sub>2</sub> adsorption/desorption measurements. The obtained catalysts were investigated for hydration of CO<sub>2</sub> and its precipitation as CaCO<sub>3</sub> at room temperature. We investigated the effect of synthesis method and cationic template on catalytic activity of Zn/MCM-41 catalysts. The results showed that template containing Zn/MCM-41 prepared by template ion exchange technique has high CO<sub>2</sub> hydration activity. This high activity is due to the presence of strong basic sites. It was also found that this catalyst can be easily recovered from the reaction mixture and reused without activation.

**Keywords:** Zn/MCM-41, template, CO<sub>2</sub> capture, CaCO<sub>3</sub>

### Introduction

Human and industrial development over the past hundred years has led to a huge increase in fossil fuel consumption and CO<sub>2</sub> emissions, causing a dramatic increase in atmospheric CO<sub>2</sub> concentration. This increased CO<sub>2</sub> is believed to be responsible for a significant rise in global temperature over the past several decades. In an attempt to solve these problems, researchers have proposed the large-scale sequestration of CO<sub>2</sub> from our atmosphere. Mineral carbonation aims to create stable carbonate minerals such as magnesite (MgCO<sub>3</sub>) and calcite (CaCO<sub>3</sub>) by reacting CO<sub>2</sub> with silicate minerals containing magnesium and calcium.<sup>1</sup> Such minerals are stable over geologic timescales, so sequestration by this method would minimize risk of leaking back into the atmosphere in the future. Furthermore, the resulting material could be used as a building material, as an additive to concrete or paper, or as a soil amendment to improve texture, pH and fertility of low-productivity soils.

The zinc-containing enzyme carbonic anhydrase catalyzes the reversible hydration of CO<sub>2</sub> to bicarbonate.<sup>2</sup> Actually, after CO<sub>2</sub> binding, the zinc-bound hydroxide (ZnOH) nucleophilically attacks the CO<sub>2</sub> to form

bicarbonate. Then, a molecule of water coordinates directly to the zinc ion, which promotes diffusion of the bicarbonate out of the active site. Finally, the active site is regenerated by the removal of H<sup>+</sup> from the active site to a proton-transfer group, then to buffer, and finally to solvent (proton wire). This reaction is made possible by the amphiphilic active site of this enzyme. That is, on one side is a hydrophobic patch which is responsible for the binding of carbon dioxide. On the other side is a patch of hydrophilic residues that act to orient the CO<sub>2</sub> and also form the aforementioned proton wire.<sup>3</sup>

Porous solids such as zeolites,<sup>4</sup> activated carbon<sup>5</sup> and metal organic frameworks<sup>6</sup> are good candidates for capturing CO<sub>2</sub> through physical adsorption. The physical adsorption process that requires less energy is cost effective and is easy to handle in a wide range of temperatures and pressures. Recently, MCM-41 gained special interest for CO<sub>2</sub> adsorption due to its high porosity and surface area to facilitate rapid gas diffusion to and from their surface.<sup>7,8</sup> MCM-41 is synthesized from the surfactant micellar template addition of an inorganic silica source. As surfactants are amphiphilic, they contain both hydrophobic and hydrophilic groups. Furthermore, template-containing MCM-41 molecular sieve possesses highly basic sites.<sup>9,10</sup> On the other hand, zinc plays an important role in the activity of carbonic anhydrase. So we assumed that the

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combination of template and zinc could increase the rate of CO<sub>2</sub> hydration reaction.

In the present study, we have synthesized Zn/MCM-41 catalysts by three different metal loading methods. In order to compare the effect of the template, a series of as-synthesized molecular sieves, containing their organic template, were also tested for CO<sub>2</sub> hydration. Reusability of recovered catalysts was also measured.

## Experimental

Tetraethyl orthosilicate (> 98%), cetyltrimethylammonium bromide (≥ 98%), tris(hydroxymethyl)aminomethane (≥ 99%) and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (≥ 98.5) were purchased from Merck and used as received. X-Ray diffraction (XRD) measurements were performed on a Philips-PW 17C diffractometer with Cu K<sub>α</sub> radiation. The elemental chemical compositions of the samples were determined by energy-dispersive X-ray spectroscopy (EDX) (VEGA\TESCAN-LMU, Czech Republic) under vacuum mode. Fourier transform infrared (FTIR) spectra were recorded on a Tensor 27 (Bruker Inc., Germany) instrument using KBr pressed powder discs. A Mettler Toledo thermogravimetry (TG/SDTA 851, Switzerland) was used for thermogravimetric analysis (TGA). A Nova 2200, Version 7.11 (Quantachrome Inc., USA) adsorption apparatus was used for specific surface-area evaluation.

### Catalyst preparation

#### Direct synthesis (DS) method

In a typical non-hydrothermal synthesis,<sup>11</sup> 0.2 g (0.52 mmol) of cetyltrimethylammonium bromide (CTAB) were dissolved in 96 mL of NaOH aqueous solution (15.0 mmol L<sup>-1</sup>), followed by a dropwise addition of 1 mL (4.48 mmol) of tetraethyl orthosilicate (TEOS). Then, 0.27 g of zinc nitrate powder (0.9 mmol) was slowly added. The mixture was vigorously stirred and heated to 80 °C for 2 h. Subsequently, the hot solution was filtered and the isolated product washed with deionized water and dried at ambient temperature. In some preparations the cationic surfactant was removed by calcination in air at 640 °C for 6 h.

#### Template ion exchange (TIE) method

MCM-41 was synthesized by the above mentioned procedure, but without the introducing of zinc salt. Then the as-synthesized MCM-41 (0.34 g) was introduced into a Zn(NO<sub>3</sub>)<sub>2</sub> aqueous solution (containing 0.27 g of zinc salt) and stirred for 3 h. After the ion exchange procedure, the solid was recovered by filtration and then washed with deionized water, followed by drying in air at ambient

temperature. In some preparations the cationic surfactant was removed by calcination in air at 640 °C for 6 h.

#### Wet impregnation (WI) method

The calcined MCM-41 sample was introduced into a calculated amount of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution (0.27 g). After 1 h, the resultant mixture was dried at 80 °C.

#### Calcium carbonate deposition

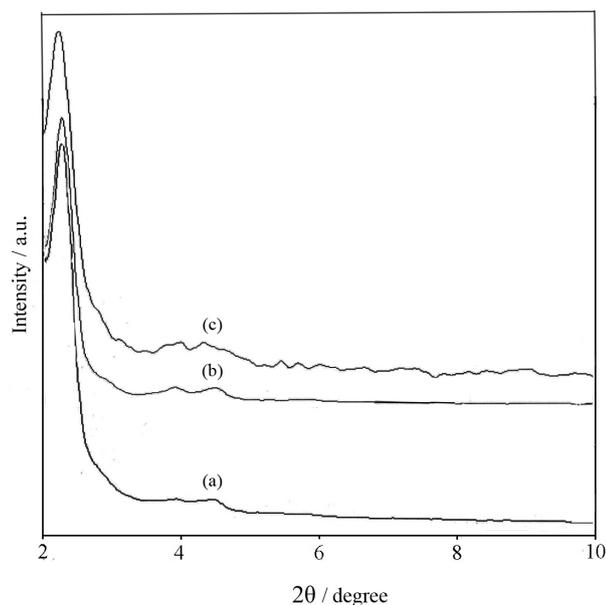
The precipitation experiments was performed by the method described in the literature,<sup>12,13</sup> with some modification. CO<sub>2</sub> hydration was conducted at 25 °C in the presence of 100 mg of Zn/MCM-41 that dispersed in 10 mL of 1.0 M Tris-HCl buffer (pH 8.0). The catalyst suspension was then added to 100 mL of a saturated CO<sub>2</sub> solution (130 mL CO<sub>2</sub>; measured using soda lime).<sup>14</sup> CO<sub>2</sub> hydration was determined to be complete within 10 min because the pH stabilized at a constant value. The hydrated solution of CO<sub>2</sub> was filtered to recover the Zn/MCM-41 catalyst for the next cycle and then the filtrate was treated with 20 mL of 4% CaCl<sub>2</sub> solution at pH 10.0. After 120 min, the precipitated CaCO<sub>3</sub> was filtered, dried at 60 °C and weighed. The entire experiment was repeated three times.

## Results and Discussion

### Characterization

As previously indicated, the absence of the hydrothermal step in the synthesis modifies the structural and textural characteristics of the MCM-41 support.<sup>15</sup> For the samples studied, the specific surface area and the mesopore wall thickness decreased with increasing time and temperature of the hydrothermal treatment. In our work, all MCM-41 samples were prepared via non-hydrothermal procedure.

The low angle XRD patterns of MCM-41 exhibit four well-resolved peaks with a very intense diffraction peak (100) at 2θ ca. 2.5 and three peaks with lower intensity at higher degree (3-5°), which were indexed to the 110, 200, and 210 planes characteristic for textural uniformity of the hexagonal p6mm structure.<sup>16</sup> All Zn/MCM-41 samples show a typical peak at 2θ = 2.4° and two additional weak peaks (Figure 1). Despite the weakness of reflections of higher order indices, the major reflection (100) was retained in the zinc substituted silica materials. This implies that the mesoporous structure of MCM-41 was preserved. However, Zn/MCM-41 (WI) changed into more disordered structure after incorporation in comparison with Zn/MCM-41 (TIE) and Zn/MCM-41 (DS), since the whole metal precursor retained on the support surface.



**Figure 1.** XRD Patterns of calcined (a) Zn/MCM-41 (DS); (b) Zn/MCM-41 (TIE) and (c) Zn/MCM-41 (WI).

The scanning electron microscope (SEM) images of all Zn/MCM-41 catalysts prepared by DS, TIE and WI methods showed that all samples are spherically shaped (see Supplementary Information, Figures S1-S5), however, the particle size of template-containing catalysts is much smaller.

#### Influence of the zinc incorporation technique

Most attempts to introduce surface-bound active sites have centered on aqueous impregnation methods. Wet impregnation involves bringing the solution into the pore space of the support; by this technique, the whole precursor is expected to be retained on the support after drying. The weak interaction of metal ions with silica wall does not impede leaching of active species from the support; therefore, the catalysts prepared by wet impregnation have a limited reusability. To avoid this problem, we used other methods for incorporating the metal into the MCM-41, direct synthesis and template ion exchange, to determine the best technique for incorporating the metal into the MCM-41. The elemental concentration distribution on the catalyst is reported in Table 1. EDX results showed that using WI method high metal loading can be attained, because there is no intermediate washing step involved in this method, in contrast to the ion-exchange and direct synthesis procedure. Moreover, in the direct approach, metal precursor is introduced directly into the synthesis mixture at the beginning of preparation process; while during the template ion exchange process, the metal ions are added into the template-containing MCM-41. The

zinc content lower than 2 wt.% may arise from the pore blockage with surfactant. To confirm this hypothesis, we investigated the zinc content of the sample prepared by impregnation method. In this method, the metal salt solution is added to the support after template removal. The amount of zinc incorporated into the MCM-41 determined was 14.33, which confirmed our claim. On the other hand, the metal located inside the framework of MCM-41 was stable toward leaching, whereas the metal in extra framework position leached out to the reaction medium. Therefore, direct synthesis is the best method for metal incorporation into MCM-41.

**Table 1.** The zinc content and surface area of Zn/MCM-41 catalysts

	Catalyst	Zn <sup>a</sup> / wt.%	S <sub>BET</sub> / (m <sup>2</sup> g <sup>-1</sup> )
1	[CTA]Zn/MCM-41 (DS)	11.02	79
2	calcined Zn/MCM-41 (DS)	11.29	600
3	[CTA]Zn/MCM-41 (TIE)	1.16	39
4	calcined Zn/MCM-41 (TIE)	1.23	542
5	Zn/MCM-41 (WI)	14.33	309

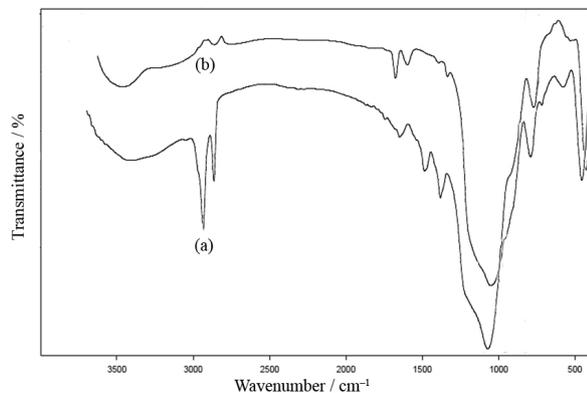
<sup>a</sup>Determined by EDX analysis.

#### Template removal

Cetyltrimethylammonium bromide is the most commonly used template in MCM-41 synthesis. It is necessary to remove the occluded organic molecules to prepare the sieves porous for adsorption and catalysis. In general, the template molecules are burned off by calcination at 500-600 °C in air or oxygen. A series of as-synthesized molecular sieves were also utilized for CO<sub>2</sub> hydration.

Figure 2 shows the FTIR spectra of template-containing Zn/MCM-41 and calcined Zn/MCM-41 prepared by direct synthesis method. The broad transmission band at approximately 3400 cm<sup>-1</sup> could be attributed to surface silanols and adsorbed water molecules. The asymmetric Si–O–Si stretching vibration modes appear at 1030 and 1070 cm<sup>-1</sup>. The symmetric stretching mode occurs at 800 cm<sup>-1</sup>, while the band at 455-460 cm<sup>-1</sup> is assigned to the Si–O–Si bending mode.<sup>17</sup> The [CTA]Zn/MCM-41 sample (Figure 2a) exhibits absorption bands around 2970 and 2927 cm<sup>-1</sup>, corresponding to C–H stretch vibrations of the surfactant molecules which are absent in calcined Zn/MCM-41. The peaks at 1620-1630 cm<sup>-1</sup> are assigned to vibrations of hydroxyl groups. The template containing sample also shows an absorption band at 1382 cm<sup>-1</sup> that is absent in the calcined Zn/MCM-41. This could be attributed to the vibration of N–O of nitrate. The values of specific surface area (S<sub>BET</sub>) of the Zn/MCM-41 molecular

sieves before and after calcination (Table 1) confirm that the specific surface area of the as-synthesized molecular sieves is not higher than  $79 \text{ m}^2 \text{ g}^{-1}$  as a consequence of pore filling by the surfactant CTAB



**Figure 2.** FTIR spectra of (a) [CTA]Zn/MCM-41 (DS) and (b) calcined Zn/MCM-41 (DS).

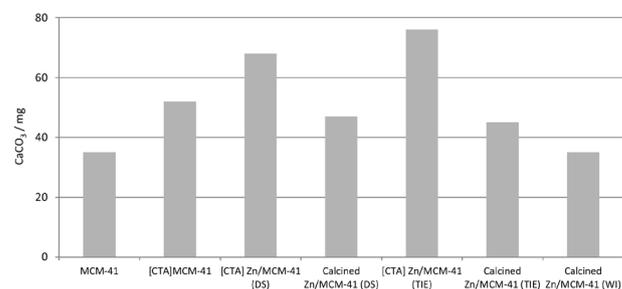
#### Hydration and sequestration of $\text{CO}_2$

There are some reports about immobilization of native carbonic anhydrase on mesoporous material; Vinoba *et al.* performed a series of experiments about immobilization of carbonic anhydrase (CA) onto mesoporous SBA-15,<sup>19</sup> nanosilver supported SBA-15,<sup>20</sup> and Au nanoparticles assembled onto amine/thiol-functionalized mesoporous SBA-15<sup>21</sup> for  $\text{CO}_2$  sequestration. For example, the amount of  $\text{CaCO}_3$  precipitated over CA/Au/MPTES/SBA-15 was nearly the same as that precipitated over free CA and the catalyst retained its activity even after 20 days storage at  $25^\circ\text{C}$  and 20 recycling runs. In 2012, carbonic anhydrase enzyme was immobilized in ordered mesoporous aluminosilicates (AIKIT-5) by Wanjari *et al.*<sup>22</sup> The  $\text{CO}_2$  sequestration capacity of prepared catalyst showed  $16.14 \text{ mg}$  of  $\text{CaCO}_3$  per mg of CA compared to  $33.08 \text{ mg}$  of  $\text{CaCO}_3$  per mg of CA for free CA.<sup>22</sup> It can be seen from the literature overview that no research has been conducted into mimicking the active site of carbonic anhydrase based on mesoporous material. Therefore, we prepared Zn/MCM-41 by three approaches and investigated the effect of surfactant which serves as template for the MCM-41 synthesis.

The ability of catalysts to sequester  $\text{CO}_2$  was tested by incubating them in water saturated with  $\text{CO}_2$  (Figure 3). Despite the very low specific surface area (Table 1), the template-containing Zn/MCM-41 showed a much higher catalytic activity in hydration of  $\text{CO}_2$  relative to calcined catalysts; the amount of  $\text{CaCO}_3$  precipitation in the presence of [CTA]Zn/MCM-41 and calcined Zn/MCM-41 for catalysts prepared by direct synthesis

was 68 and 47 mg, respectively. When using [CTA] MCM-41 catalysts in the Knoevenagel condensation, Kubota *et al.*<sup>9,10</sup> suggested that the basic sites are  $\equiv\text{SiO}^-$  siloxy anions, interacting with  $\text{CTA}^+$  cations. Consequently, the Lewis basicity of the Si–O oxygen atom, belonging to [CTA]MCM-41 sample, is much higher. It is the reason that template-containing catalysts exhibited more activity than their calcined counterparts. Moreover, in spite of the small incorporation of zinc to the mesoporous MCM-41 by TIE approach compared to DS method, the catalysts prepared by template-ion exchange method produced larger amounts of  $\text{CaCO}_3$ . It seems that zinc has negative effect on catalyst activity, although carbonic anhydrase that catalyses  $\text{CO}_2$  hydration contains Zn atom. One of the reasons could be the zinc being coordinated by three amino acid ligands in the natural enzyme and these *N*-ligands lower the  $\text{p}K_a$  of the bound  $\text{H}_2\text{O}$  compared to the free  $\text{H}_2\text{O}$ , creating a high local concentration of  $\text{OH}^-$  as attacking nucleophile.<sup>23</sup>

The higher activity of template-containing catalysts in comparison to calcined analogue confirmed this finding.



**Figure 3.** Activity of Zn/MCM-41 catalysts in  $\text{CO}_2$  hydration.

The high catalytic activity of catalysts prepared by TIE method compared to directly synthesized catalysts could be explained by thermogravimetric analysis. The TGA-DTA curves of the as-synthesized Zn/MCM-41 (DS) and Zn/MCM-41 (TIE) are shown in Figures 4 and 5, respectively. Three distinct stages of weight loss were observed in template-containing Zn/MCM-41:  $20\text{--}150^\circ\text{C}$  (due to desorption of water),  $150\text{--}450^\circ\text{C}$  (due to decomposition of the template) and above  $450^\circ\text{C}$  (due to water loss via condensation of silanol groups to form siloxane bonds). The amount of template could therefore be estimated from the weight loss between  $150$  and  $450^\circ\text{C}$ . These amounts were approximately 30 and 36% for [CTA]Zn/MCM-41 prepared by DS and TIE methods, respectively. These data indicated that the ionic template amount is higher for the catalysts prepared by template ion exchange than for the catalysts prepared by direct synthesis approach that improves their  $\text{CO}_2$  capture capability.

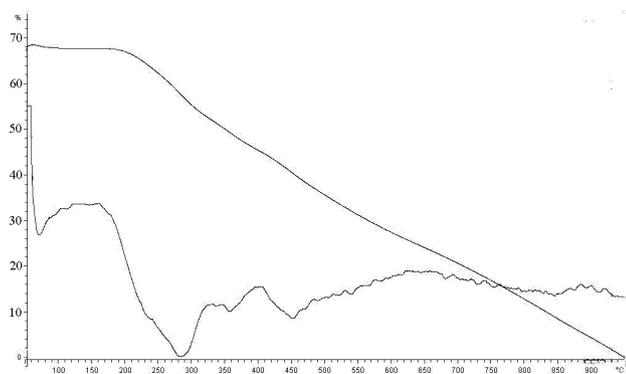


Figure 4. TGA and DTA measurement of [CTA]Zn/MCM-41 (DS).

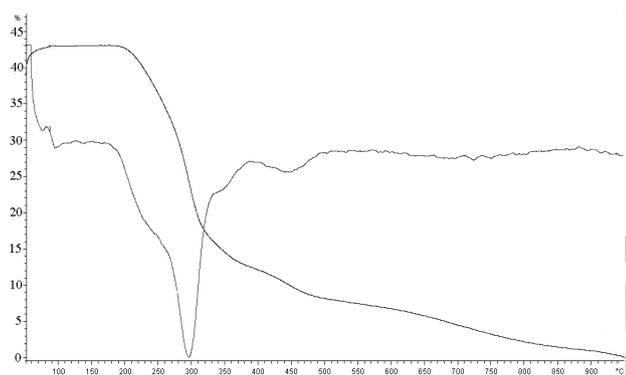


Figure 5. TGA and DTA measurement of [CTA]Zn/MCM-41 (TIE).

### Calcium carbonate characterization

The formation of calcite was confirmed via X-ray powder diffraction. XRD analysis of CaCO<sub>3</sub> precipitated from the hydrated CO<sub>2</sub> prepared by the as-synthesized Zn/MCM-41 showed sharp peaks at  $2\theta = 29.3, 39.4$  and  $48.2^\circ$  (Figure 6a). Calcium carbonate has three crystal phases (calcite, aragonite, and vaterite). The calcite phase is a thermodynamically most stable phase under the ambient conditions. The XRD pattern of precipitates match with structural reports for calcite.<sup>24</sup> Furthermore, the FTIR spectrum of CaCO<sub>3</sub> crystals is shown in Figure 6b. It was observed that two characteristic peaks of calcite occurred at  $872$  and  $710\text{ cm}^{-1}$ .<sup>25</sup>

### Reusability

One of the most important features of a solid catalyst is the ability to be recycled. After each experiment the catalyst was separated by filtration, washed, and reused for next runs without activation. The precipitated CaCO<sub>3</sub> was recovered by filtration and weighed. The results are given in Figure 7. Surprisingly, all recovered catalysts exhibited higher activity in the CO<sub>2</sub> hydration reaction. This result may arise from the enhanced basicity of the catalysts after

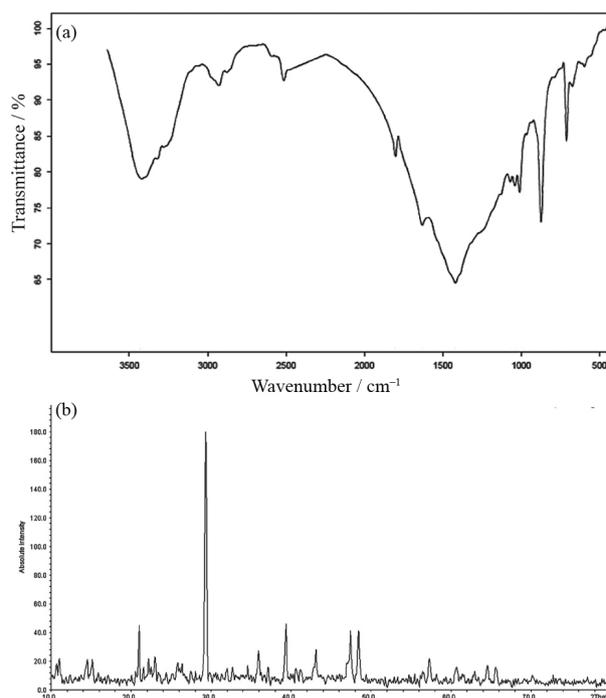


Figure 6. XRD pattern (a) and FTIR spectrum (b) of precipitated calcium carbonate by Zn/MCM-41 catalysts.

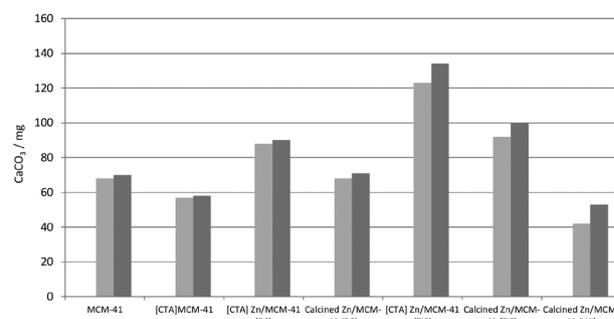


Figure 7. Reusability (second and third run) of Zn/MCM-41 catalysts for CO<sub>2</sub> hydration.

the first use. However, after second run the activity did not change significantly (Table 2).

EDX analysis was performed to estimate the zinc content of the recovered samples (Table 3). These results indicated that partial leaching of the zinc from supports prepared by DS method occurs under the reaction condition (5%). However, there was significant leaching of the zinc from catalysts prepared via TIE and WI approaches (19 and 40%, respectively).

Infrared spectroscopy was performed to investigate the leaching of organic template from recovered catalysts (Figure 8a compared to Figure 2a). The C–H stretching bands at  $2924$  and  $2853\text{ cm}^{-1}$  and its vibration mode observed at  $1471\text{ cm}^{-1}$  are similar to that of catalysts, which confirms that the organic compound has not been removed. Consequently, the CTA molecules are not so easily leached

**Table 2.** Reusability of [CTA]Zn/MCM-41 catalyst for CO<sub>2</sub> hydration

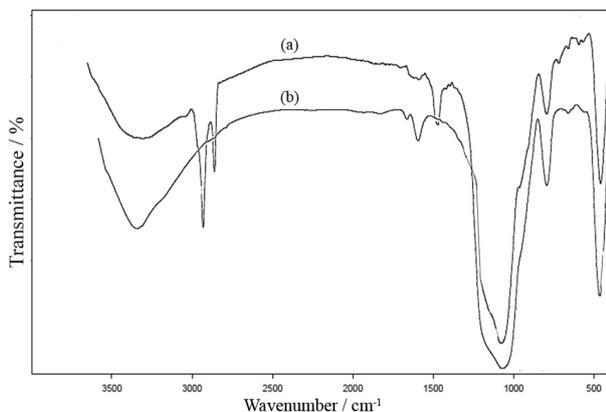
	Run					
	1	2	3	4	5	6
CaCO <sub>3</sub> / mg	76	123	134	132	134	136

**Table 3.** The amount of zinc in recovered Zn/MCM-41 catalysts

Catalyst	Zn <sup>a</sup> / wt. %
[CTA]Zn/MCM-41 (DS)	10.42
calcined Zn/MCM-41 (DS)	10.50
[CTA]Zn/MCM-41 (TIE)	0.94
calcined Zn/MCM-41 (TIE)	1.01
Zn/MCM-41 (WI)	8.51

<sup>a</sup>Determined by EDX analysis.

during the CO<sub>2</sub> hydration process because they are more stable, as a consequence of the strong electrostatic forces between the CTAB template and silica wall. Furthermore, based on FTIR spectra of recovered template-containing and calcined Zn/MCM-41, there is no evidence for CO<sub>2</sub> adsorption on the surface of the porous support, because there is no peak at about 1400 cm<sup>-1</sup> which corresponds to the (O–C–O) symmetric stretch in HCO<sub>3</sub><sup>-</sup>.

**Figure 8.** FTIR spectra of recovered (a) [CTA]Zn/MCM-41 and (b) calcined Zn/MCM-41 prepared by direct synthesis approach.

## Conclusion

In the present study, the use of the direct synthesis, template ion exchange and impregnation methods for preparing zinc-incorporated MCM-41 leads to catalysts with different catalytic properties towards the CO<sub>2</sub> hydration. The results showed that template-containing Zn/MCM-41, prepared by TIE approach, was the most active catalyst for this process, which could be attributed to the presence of basic template. This catalyst is insoluble and

therefore could be separated simply by filtration. Hence, [CTA]Zn/MCM-41 (TIE) provides a green, stable, reusable, and convenient catalyst for CO<sub>2</sub> sequestration, and produces pure calcite phase CaCO<sub>3</sub>.

## Supplementary Information

Supplementary data are available free of charge at <http://jbs.sbq.org.br> as PDF file.

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## References

- Oelkers, E. H.; Gislason, S. R.; Matter, J.; *Elements* **2008**, *4*, 333.
- Liang, J. Y.; Lipscomb, W. N.; *Biochemistry* **1988**, *27*, 8676.
- Domsic, J. F.; McKenna, R.; *Biochim. Biophys. Acta* **2010**, *1804*, 326.
- Liu, Z.; Grande, C. A.; Li, P.; Yu, J.; Rodrigues, E.; *Sep. Sci. Technol.* **2011**, *46*, 434.
- Guo, B.; Chang, L.; Xie, K.; *J. Nat. Gas Chem.* **2006**, *15*, 223.
- Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T. H.; Long, J. R.; *Chem. Rev.* **2012**, *112*, 724.
- Branton, P. K.; Hall, G.; Treguer, M.; Sing, K. S. W.; *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2041.
- Belmabkhout, Y.; Sayari, A.; *Adsorption* **2009**, *15*, 318.
- Kubota, Y.; Nishizaki, Y.; Ikeya, H.; Saeki, M.; Hida, T.; Kawazu, S.; Yoshida, M.; Fujii, H.; Sugi, Y.; *Microporous Mesoporous Mater.* **2004**, *70*, 135.
- Kubota, Y.; Ikeya, H.; Sugi, Y.; Yamada, T.; Tatsumi, T.; *J. Mol. Catal. A: Chem.* **2006**, *249*, 181.
- Tantirungrotechai, J.; Thananupappaisal, P.; Yoosuk, B.; Viriyempikul, N.; Faungnawakij, K.; *Catal. Commun.* **2011**, *16*, 25.
- Mirjafari, P.; Asghari, K.; Mahinpey, N.; *Ind. Eng. Chem. Res.* **2007**, *46*, 921.
- Li, W.; Chen, W. S.; Zhou, P. P.; Cao, L.; Yu, L. J.; *Colloids Surf., B* **2013**, *102*, 281.
- Johnson, M. S.; Lehmann, J.; Guimaraes Couto, E.; *Oecol. Bras.* **2008**, *12*, 85.
- Ribeiro Carrott, M. M. L.; Estêvão Candeias, A. J.; Carrott, P. J. M.; Unger, K. K.; *Langmuir* **1999**, *15*, 8895.
- Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S.; *Nature* **1992**, *359*, 710.
- Broyer, M.; Valange, S.; Bellat, J. P.; Bertrand, O.; Weber, G.; Gabelica, Z.; *Langmuir* **2002**, *18*, 5083.

18. Kim, S.; Ida, J.; Gulians, V. V.; Lin, J. Y. S.; *J. Phys. Chem. B* **2005**, *109*, 6287.
19. Vinoba, M.; Bhagiyalakshmi, M.; Jeong, S. K.; Yoon, Y. I.; Nam, S. C.; *Colloids Surf., B* **2012**, *90*, 91.
20. Vinoba, M.; Bhagiyalakshmi, M.; Jeong, S. K.; Yoon, Y. I.; Nam, S. C.; *J. Mol. Catal. B: Enzym.* **2012**, *75*, 60.
21. Vinoba, M.; Lim, K. S.; Lee, S. H.; Jeong, S. K.; Alagar, M.; *Langmuir* **2011**, *27*, 6227.
22. Wanjari, S.; Prabhu, C.; Satyanarayana, T.; Vinu, A.; Rayalu, S.; *Microporous Mesoporous Mater.* **2012**, *160*, 151.
23. Silverm, D. N.; *Can. J. Bot.* **1991**, *69*, 1070.
24. Zhang, F.; Wang, J.; Hou, Z.; Yu, M.; Xie, L.; *Mater. Des.* **2006**, *27*, 422.
25. Lose, E.; Wilson, R. M.; Seshadri, R.; Meldrum, F. C.; *J. Cryst. Growth* **2003**, *254* 206.

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