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CO_2 capture over amine-functionalized MCM-22, MCM-36 and ITQ-2

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ABSTRACT

MCM-22 and its related structures MCM-36 and ITQ-2, as well as Fe-substituted MCM-22 (Fe-MCM-22), were synthesized and evaluated collectively as a CO_2 capturing agent with or without post-synthesis amine (NH_2)-functionalization. The amount of the grafted amine was measured by elemental analysis (EA), and the corresponding properties of the zeolite samples were examined by XRD, SEM, and BET surface area measurement. CO_2 adsorption isotherms of the zeolites were obtained at 273, 298, and 303 K, and the corresponding heats of adsorption were estimated by the Clausius–Clapeyron equation. CO_2 adsorption capacity varied in the sequence of MCM-22 (2.09) > NH_2-ITQ-2 (1.73) > ITQ-2 (1.64) > NH_2-MCM-22 (1.52) > MCM-36 (1.32) > NH_2-MCM-36 (1.20) > Fe-MCM-22 (1.20 mmol/g) at 298 K. For the zeolites without amine-grafting, aluminum content was the governing factor determining the adsorption capacity. Fe-MCM-22 resulted in low CO_2 adsorption due to its low surface area. Amine-grafting on zeolites in general resulted in an enhancement in CO_2/N_2 selectivity and increased heats of CO_2 adsorption at the expense of reduction in CO_2 capture capacity. NH_2-ITQ-2 showed exceptionally high CO_2/N_2 selectivity (10.8) accompanied by the best separation capacity (0.88 mmol/g) among the samples in the fixed bed breakthrough curve analyses. Cyclic CO_2 adsorption–desorption performance of the samples were examined by TGA in a flow system, and were found to exhibit stable cyclic runs.

1. Introduction

Carbon dioxide is the major greenhouse gas causing global warming. At the moment, the most widely accepted CO_2 capture strategy is via gas absorption, monoethanol amine (MEA) being the most widely used chemical solvent. The current liquid amine-based system for CO_2 removal, however, need remedies for corrosion and a high energy requirement for solvent regeneration [1]; carbon dioxide adsorption and separation using a variety of porous solids has received much attention in the last decades as an alternative [2]. Among the porous materials, zeolites are being investigated widely due to their high thermal stability and uniform microporous structure, along with their large internal surface area [3–8].

The attributes of the structural features in zeolites for carbon dioxide adsorption was previously discussed by Bonenfant et al. [9] and others, which included (1) the basic properties generated by the different electron densities of the framework [10], (2) polarizing power of the exchangeable cations [11–14], (3) the Si/Al ratio in zeolites, and (4) the pore size effect in zeolites. Other than these attributes, CO_2 adsorption by zeolites can also be influenced by particle morphology or isomorphous substitution of metal sites.

Fig. 1 shows the schematic structural relationship between MCM-22 and its derivatives [15]. The starting precursor, MCM-22(P), is a lamellar structure composed of 10 MR channels, and a three-dimensional MCM-22 is formed after removing organic template molecules by calcination. MCM-22 is a zeolite constructed of 10-membered sinusoidal channels and 12-membered supercages, which are located independently next to each other in a three dimensional arrangement, whereas MCM-36 is a unique zeolite with a mesoporous region generated by the expansion of the MCM-22 inter-layers via swelling/pillaring. Finally, ITQ-2 is synthesized by exfoliation of swollen MCM-22 by sonication; the nanostructure obtained can afford reactants nearly unlimited access to the external active sites [16].

Domínguez et al. [12] measured the CO_2 adsorption isotherm of ion-exchanged MCM-22 at 273 K and concluded that CO_2 adsorption capacity closely depends of the charge compensating cation. Pawlesa et al. [13] investigated the CO_2 adsorption capacity on ion-exchanged MCM-22 with different Si/Al ratios. The highest CO_2 adsorption capacity was obtained on the MCM-22 with the lowest Si/Al molar ratio and Li^+ or K^+ cations. The CO_2 adsorption capacity decreased as follows: $K^+ > Li^+ > Na^+ > Cs^+$ [14]. Synthesis of a Fe-substituted MCM-22 was also reported [17]. Isomorphous substitution in zeolites involves replacing the standard Si and Al sites with various other metal ions, which can offer materials with different electronic and textural properties and thus can affect adsorption and catalytic behavior [18].

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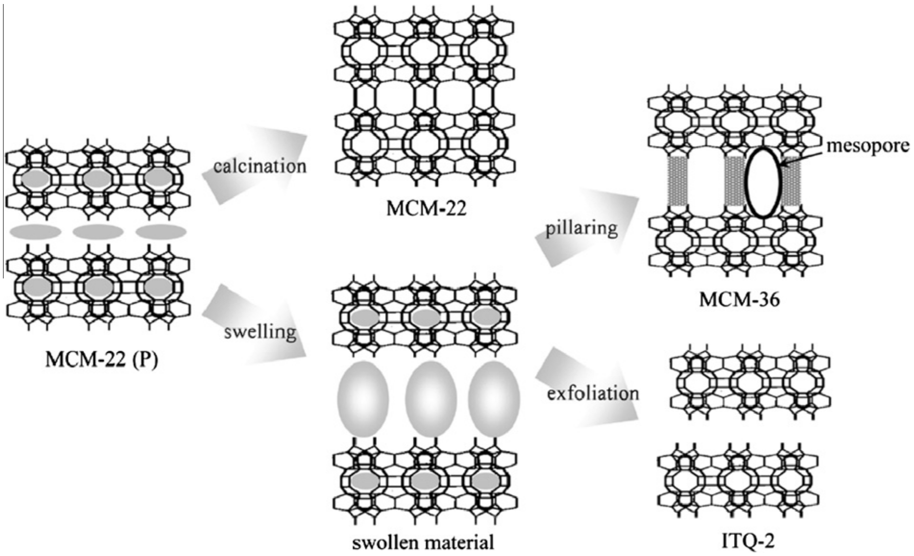

Fig. 1. Schematic representation of MCM-22, MCM-36 and ITQ-2 [15].

In order to enhance the adsorption performance of a porous adsorbent to CO_2, post-synthesis amine grafting has been applied to mesoporous silica [19], mesoporous alumina [20], and zeolite [11,21–23]. The amine-modified mesoporous sorbents yield the advantages of high selectivity to CO_2 adsorption together with a high diffusion rate of gases within the mesopores [21]. For zeolites, Zukal et al. [11] synthesized amine-grafted ITQ-6 for CO_2 separation; they also compared the adsorption properties of the prepared materials toward CO_2 with those of amine-functionalized mesoporous SBA-15. Experimentally determined efficiencies of amine ligands in ITQ-6 indicated that adsorption of CO_2 occurs simultaneously on both amine ligands and on the bare zeolite surface. According to Nik et al. [21], 3-aminopropyldimethylethoxysilane-grafted FAU/EMT using isopropanol showed a substantial reduction in adsorption capacity compared to the parent zeolites because of partial blockage of zeolite pores by aminosilane molecules after grafting. Pechar et al. [22] measured the CO_2 and N_2 adsorption isotherms of amine-functionalized zeolite L at 308 K and concluded, interestingly, that CO_2 adsorption capacity decreased with lower CO_2/N_2 selectivity.

In this work, we investigated in a systematic manner the effects of structure, isomorphous substitution, and amine-functionalization on CO_2 adsorption using MCM-22, MCM-36, and ITQ-2, all of which can be prepared from the same synthesis precursor. We measured the CO_2 adsorption capacities of the prepared sample using both static and flow systems. The heats of adsorption and CO_2 selectivity over N_2 were estimated using the adsorption isotherms. CO_2 adsorption kinetics were also examined by breakthrough experiments; investigations into breakthrough behavior in a flow system would provide useful Supplementary data to compare the sorption capacity and adsorption selectivity in zeolite adsorbents. The stability of the prepared sample was tested by recycle runs. Investigation of the desorption properties in the adsorbent was conducted first to determine suitable regeneration conditions.

2. Experimental

2.1. Synthesis of MCM-22, MCM-36, ITQ-2, and Fe-MCM-22

MCM-22 was synthesized based on the recipe reported by Ravishankar et al. [24]. Initially, 43.89 g of sodium silicate (26.5% SiO_2, 10.6% Na_2O, 62.9% H_2O, Aldrich) was mixed with 22.2 g of de-ionized water. To this solution, 8.81 g of hexamethyleneimine (99%, Aldrich) was added. Then, a solution of 4.41 g of aluminum sulfate (98%, Aldrich) and 3.63 g of sulfuric acid (95%, Aldrich) in 110 g of de-ionized water were added slowly. Hydrothermal reaction was then conducted at 423 K under mechanical stirring for 80 h. The obtained product MCM-22(P) was washed with sufficient de-ionized water and dried at 393 K for 6 h. The dried product was finally calcined at 823 K for 6 h to remove the organic template.

MCM-36 was prepared using a wet cake of MCM-22(P) mixed with cetyltrimethylammonium chloride (CTMACl, 25%, Aldrich) as a swelling agent and tetrapropylammonium hydroxide (TPAOH, 40%, Aldrich) in a relative weight ratio of 1:4:1.2 MCM-22(P)/CTMACl/TPAOH [25]. Tetraethylorthosilcate (TEOS, 98%, Aldrich) was used as a pillaring agent. For the synthesis of ITQ-2 [26], the swollen MCM-22(P) was stripped apart in an ultrasound bath for 1 h. The solid phase was isolated by adding a few drops of concentrated hydrochloric acid to bring the pH of the slurry below 2, which was followed by centrifuging.

Fe-MCM-22 was prepared following the procedure of Testa et al. [17] using iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98%, Aldrich), fumed SiO_2, and hexamethylenimine (99%, Aldrich) as a template.

2.2. Amine grafting on zeolite samples

Prepared zeolite samples were dried at 343 K under vacuum overnight. Three grams of each dried material was then added to 30 ml of toluene with stirring. 1.84 g of 3-aminopropyltrimethoxysilane was then added to the mixture, stirred for 6 h at room temperature, and refluxed for 4 h at 383 K. The product was filtered, washed with ethanol, and finally dried at 343 K under vacuum. Amine-grafted zeolite samples in this work were designated as NH_2-MCM-22, NH_2-MCM-36, and NH_2-ITQ-2.

2.3. Characterization

XRD patterns of the samples were obtained on a Rigaku diffractometer (D/MAX 2200V/PC, Rigaku) using Cu Kα (λ = 1.54 Å) radiation. Nitrogen adsorption–desorption isotherms were measured on a BELSORP-mini (BEL, Japan) at 77 K. The specific surface areas of the samples were calculated by the Brunauer–Emmett–Teller