



## Two-dimensional zeolites: Adsorption of carbon dioxide on pristine materials and on materials modified by magnesium oxide



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### ABSTRACT

Magnesium oxide has been introduced into zeolites MCM-22, MCM-36, IPC-3, IPC-3PI and ITQ-2 synthesized from 2D layered precursors MCM-22P and ICP-3P. Prepared materials were tested as carbon dioxide adsorbents in the temperature range from 0 °C to 60 °C. For parent zeolites, the IPC-3 has shown at 1 kPa the adsorption capacity (5.1 cm<sup>3</sup>/g STP), which was nearly two times higher than that of MCM-22 (2.7 cm<sup>3</sup>/g STP). Adsorption capacity of zeolites in the low pressure region markedly increased due to incorporation of magnesium oxide. The amount adsorbed on MgO-IPC-3 and MgO-MCM-22 at 1 kPa was enhanced to 11.4 and 13.7 cm<sup>3</sup>/g STP. Isothermic adsorption heats giving information on the energetics of CO<sub>2</sub> adsorption were calculated.

### 1. Introduction

Control of the carbon dioxide emission has become serious problem and challenging topic because this gas is one of the major greenhouse gases, which are believed to cause global warming and weather disruptions [1]. Among the possible technologies for separation of CO<sub>2</sub> from gas mixtures, vacuum swing adsorption (VSA) is preferred mode of operation for easy to use and low energy requirements [2]. For efficient VSA process under given conditions (such as temperature and composition of the gas mixture) an important task is to find suitable adsorbents. Current effort to develop such adsorbents was focused on pristine [3,4], and modified [5] zeolites, activated carbons [6], inorganic oxides or hydroxalite like compounds [7,8], amine functionalized adsorbents [9], metal organic frameworks [10] and microporous organic polymers [11]. Detailed reviews on the CO<sub>2</sub> separation based on adsorption processes include Choi et al. [12], Spigarelli et al. [13] and Moliner et al. [14].

Among inorganic oxides, magnesium oxide has been recognized as a suitable material for CO<sub>2</sub> separation by the VSA process due to its stability, facile mass transport and low energy requirements for regeneration [15–21]. However, the magnesium oxide prepared via conventional routes (e.g. prepared by decomposition of magnesium salts or magnesium hydroxide) possesses a low BET area and a small amount of pores limiting its adsorption capacity. The activity of MgO is improved via preparation of mesoporous oxides with higher BET areas or via incorporation of this oxide into suitable support [5]. Nanoporous MgO characterized by exceptional CO<sub>2</sub> adsorption capacity under conditions

mimicking flue gas was synthesized by thermal conversion of aliphatic ligand-based metal-organic framework [7].

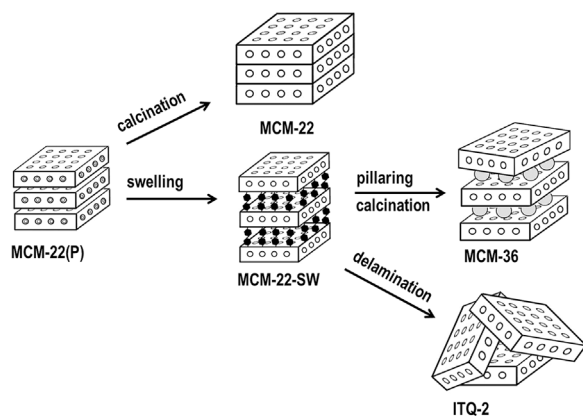
At present, hierarchical microporous-mesoporous materials based on two-dimensional zeolites (2D) gained special interest due to large BET areas, high porosity and high thermal stability. Synthesis of these zeolites from layered precursors, their post-synthesis modification or delamination and structural characterization were recently discussed in detail by Roth et al. [22]. Opanasenko et al. have reported many examples of application of 2D zeolites in catalysis [23]. It is obvious that 2D zeolites can be useful not only in catalysis but also in adsorption by porous solids. Generally, two-dimensional zeolites might represent efficient adsorbents or novel supports for different adsorptives.

Two-dimensional precursors MCM-22P [24,25], and IPC-3P [26] consisting MWW layers offer opportunity for creating new open zeolite structures. Adsorption of CO<sub>2</sub> on the zeolites prepared from MCM-22P, i.e. on MCM-22, on related structures MCM-36, ITQ-2 and ITQ-6 and on their amine-functionalized forms, was investigated by Yang et al. [27] and Zukal et al. [28]. It was found for pure zeolites that the amount of CO<sub>2</sub> adsorbed is inversely dictated by the Si/Al ratio of the sample. MCM-22 with the highest Al content attains the CO<sub>2</sub> adsorption capacity of 47 cm<sup>3</sup>/g STP at 25 °C and 101 kPa. Modification of MCM-22 by different alkali metal cations showed that the adsorption capacity depends significantly on the nature and the concentration of cations [4]. The highest adsorption capacity 60 cm<sup>3</sup>/g STP at 0 °C and 101.3 kPa was obtained with potassium form of MCM-22 with Si/Al ratio of 15 [29].

As adsorption heat represents important characteristic of the

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**Scheme 1.** Schematic representation of various derivatives obtained from MCM-22 precursor.

adsorption, the temperature dependence of CO<sub>2</sub> adsorption on MCM-22 was investigated. Derived isosteric adsorption heats revealed a decisive role of the nature of alkali metal cations [29]. Isosteric heats attain 35–40 kJ/mol with potassium form of ratio Si/Al = 15. However, the isosteric heat ranges only between 25 and 30 kJ/mol with sodium form of ratio Si/Al = 40.

In this contribution we report the carbon dioxide adsorption on parent and magnesium oxide containing zeolites MCM-22 [30] and IPC-3 [26], pillared zeolites MCM-36 [31,32], and IPC-3-PI [26] and delaminated zeolite ITQ-2 [33]. As shown in Scheme 1, the zeolites MCM-22, MCM-36, and ITQ-2 are based on the precursor MCM-22P, which was synthesized using hexamethylenimine as template as described in Ref. [34]. The MWW-zeolite was prepared by calcination of its precursor. To prepare pillared zeolite MCM-36, the precursor MCM-22P was swollen in solution of cetyltrimethylammonium hydroxide and converted into product MCM-36 with siliceous pillars by treatment with tetraethyl orthosilicate (TEOS) followed by hydrolysis. The zeolite ITQ-2 was synthesized by exfoliation of swollen precursor MCM-22P by sonication. Zeolites IPC-3 and IPC-3-PI were synthesized from the precursor IPC-3P. This novel layered precursor was obtained as an intermediate during the synthesis of TUN zeolite using 1,4-bis(*N*-methylpyrrolidinium)butane and Na<sup>+</sup> ions as structure directing agents [26]. In accordance with the Ostwald rule the precursor IPC-3P represents the least stable phase crystallizing first. (At longer synthesis time, zeolite TUN is formed as the final product of the synthesis.) The precursor IPC-3P was treated similarly as well as precursor MCM-22P. Therefore, the microporous zeolite IPC-3 was prepared by calcination of IPC-3P. The pillared IPC-3-PI zeolite was synthesized by the swelling of IPC-3P in solution of CTMA-OH and pillaring using TEOS.

To prepare adsorbents containing magnesium oxide, we have introduced this oxide into zeolites prepared from the precursors MCM-22P and IPC-3P using the method developed in Ref. [21] for mesoporous silicas. This method is based on *in situ* precipitation of magnesium oxalate followed by its conversion to magnesium oxide at 300 °C.

The structure of all materials was characterized by argon adsorption and X-ray powder diffraction. Adsorption isotherms of carbon dioxide were recorded on all materials in the temperature range 0 °C–60 °C. To show an influence of magnesium oxide on CO<sub>2</sub> adsorption, isotherms on materials containing this oxide were compared with isotherms on parent materials. Based on the temperature dependence of CO<sub>2</sub> adsorption, isosteric heats of were determined and discussed.

## 2. Experimental

### 2.1. Materials

Aluminum nitrate nonahydrate, sodium aluminate, Ludox AS-30, fumed silica, hexamethylenimine and 1,4-bis(*N*-methylpyrrolidinium)

butane, tetraethylorthosilicate (TEOS) and sodium hydroxide were purchased by Sigma-Aldrich and used as supplied. Cetyltrimethylammonium hydroxide (CTMA-OH) solution was obtained by ion exchange with AG1-X8 resin from BioRad.

### 2.2. Synthesis

Zeolites MCM-22 and MCM-36 were prepared following the protocol given in Ref. [31]. The synthesis of the zeolite ITQ-2 was performed following Ref. [33]. Syntheses of IPC-3 and IPC-3-PI are described in more detail because they are based on recently published new precursor IPC-3P.

The precursor MCM-22P was prepared using Ludox AS-30 and solid sodium aluminate as sources of silicon and aluminum, respectively. Hexamethylenimine was employed as a structure directing agent. The synthesis mixture was heated in autoclave at 143 °C under static conditions for 96 h and the product MCM-22P was isolated. MCM-22 zeolite was prepared by calcination of MCM-22P at 540 °C for 5 h. Swelling of MCM-22P was performed with CTMA-OH 20 wt.% solution. To prepare pillared material MCM-36, the swollen sample was treated with TEOS for 18 h at 85 °C under reflux. The solid was isolated and dried at room temperature. This powder was mixed with excess of water, stirred overnight, separated and dried. Calcination was performed at 540 °C for 5 h.

Zeolite ITQ-2 was prepared from the swollen MCM-22-SW. 60 mL of the slurry prepared as described above was placed in the ultrasound bath (50 W, 40 kHz) for 1 h to strip apart the layers. During the ultrasound treatment the pH of the slurry approached 12.5 and the temperature did not exceed 50 °C. The solid phase was isolated by adding a few drops of HCl.

The precursor IPC-3P is formed initially during the synthesis of the zeolite TNU-9 with 1,4-bis(*N*-methylpyrrolidinium)butane (1,4-MPB) and Na<sup>+</sup> ions as structure directing agents [26]. 1,4-MPB bromide was dissolved in distilled water followed by the addition of sodium hydroxide (NaOH) and aluminum nitrate nonahydrate – Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. Finally, the solution was mixed with fumed silica (SiO<sub>2</sub>) and stirred until homogeneous gel was formed. The synthesis was performed in a 500 mL Teflon-lined stainless steel autoclave was heated at 160 °C under agitation and autogenous pressure for 5 days. The solid product was filtered off, washed out with distilled water and dried in the oven at 80 °C overnight. IPC-3 zeolite was obtained by the calcination of IPC-3P. Swelling of IPC-3P was performed in a 100 mL flask in which 3 g of dried IPC-3P was mixed with 60 mL of CTMA-OH solution and stirred for 24 h at room temperature. After swelling, the mixture was centrifuged for 15 min followed by three-fold washing with distilled water and centrifugation for another 15 min. Finally, the solid was dried overnight at 60 °C. The swollen material was treated with TEOS for 18 h at 85 °C under reflux using 30 mL of TEOS per 1 g of the swollen sample. The solid was separated by centrifugation and dried in air at 40 °C overnight. To ensure complete hydrolysis of TEOS, the powder was treated with water (200 mL per 1 g of the sample) for 1 day. The product was centrifuged, washed with water and dried at 333 K. The obtained material was denoted IPC-3PI.

### 2.3. Preparation of MgO modified samples

In order to prepare materials containing MgO, 2 g of respective zeolite were added to solution of 5 mL of ethanol and 5 mL of distilled water containing 2 g magnesium acetate tetrahydrate. After stirring for 1 h the solid phase was separated by vacuum filtration and dried at 75 °C and 115 °C always for 1 h. After that it was soaked in 10 mL of ethanolic solution of oxalic acid (30 g of oxalic acid in 100 mL of ethanol) for 10 min. The powder was filtered, dried at 75 °C and calcined in air at 300 °C for 10 h (temperature ramp of 1 °C min<sup>-1</sup>).

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