

# Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials

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## Abstract

A series of mesoporous silica materials, MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6, was synthesized and impregnated with 50 wt% polyethyleneimine (PEI) in methanol to evaluate the performances of the materials in terms of CO<sub>2</sub> adsorption (adsorption–desorption in 150 min cycle each at 75 °C). These PEI-loaded mesoporous silica materials were characterized by XRD, N<sub>2</sub> adsorption isotherm, TGA, and TEM/SEM to monitor their textural properties before and after PEI-impregnation. All the PEI-loaded mesoporous silica samples exhibited reversible CO<sub>2</sub> adsorption–desorption behaviors with >99% recovery. The CO<sub>2</sub> adsorption capacities of the materials were substantially higher than that of pure PEI (79 mg CO<sub>2</sub>/g-adsorbent), and varied in the order of KIT-6 > SBA-16 ≈ SBA-15 > MCM-48 > MCM-41. The PEI-loaded mesoporous silica samples also showed faster adsorption kinetics than pure-PEI, and the performance of these materials as a CO<sub>2</sub> adsorbent was influenced primarily by their pore size. KIT-6 with the largest pores in 3D arrangement was impregnated with 50 wt% PEI, and showed the highest CO<sub>2</sub> adsorption capacity (135 mg/g-adsorbent) in the fastest response time. It also exhibited stable adsorption–desorption behavior in three consecutive test cycles in 900 min.

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## 1. Introduction

CO<sub>2</sub> is the major greenhouse gas causing global warming. Accordingly, there has been growing interest in developing technologies for efficient capturing and sequestration of large quantities of CO<sub>2</sub>, including the injection of captured CO<sub>2</sub> gas into a suitable geologic formation. At present, the removal and recovery of CO<sub>2</sub> from power plant flue gas is considered to be the most effective way to reduce global CO<sub>2</sub> emissions from an energy point of view. Despite various feasible processes available for CO<sub>2</sub> removal, the capture cost remains the most expensive component, and the major obstacle in CO<sub>2</sub> capture is the dynamic efficiency of the separation medium being employed [1].

Currently, large-scale separation of CO<sub>2</sub> by liquid phase amine-based absorption is in commercial operation throughout the world. But sorption processes based on solid adsorbents are also being actively pursued at present. In general, these solid phase sorbents for CO<sub>2</sub> capturing can be classified into three groups: (1) basic oxide and hydrotalcite materials via chemisorption or a chemical reaction mechanism at relatively high operating temperature; (2) inorganic porous materials such as zeolite and carbon via physisorption in micropores for low temperature application; and (3) porous hybrid materials such as metal organic frameworks (MOFs) utilizing the high gas storage capacity of the material at ambient temperature and high pressure conditions.

For high temperature applications, Ding and Alpay [2] reported moderate CO<sub>2</sub> adsorption capacities of 28.6 and 25.5 mg/g-adsorbent, respectively, on hydrotalcite at 400 and 480 °C. Song et al. [3] studied CaO-modified silica and

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reported a CO<sub>2</sub> adsorption capacity of 36.9 mg/g-adsorbent at 25 °C under 1 atm of CO<sub>2</sub>. Liang and Harrison [4] reported sodium oxide-based adsorbents for CO<sub>2</sub> chemisorption, and limestone derived adsorbents were also reported by Hughes et al. [5]. Reddy and Smirniotis [6] observed very high CO<sub>2</sub> adsorption capacity on Cs-doped CaO. Most of these basic oxide adsorbents utilize chemical reactions with CO<sub>2</sub> at high temperature and generally suffer from either low CO<sub>2</sub> capture capacities or severe energy penalties because of high desorption temperature [2–6].

Porous solid adsorbents have been widely investigated as a medium for CO<sub>2</sub> separation. Among these adsorbents, zeolites 4A, 13X, ZSM-5 [7–14], and activated carbons [15–17] have been considered for low temperature applications. Siriwardane et al. [15] reported that CO<sub>2</sub> adsorption capacity for zeolite 13X, 4A, and activated carbon at 25 °C and 1 atm CO<sub>2</sub> partial pressure are ca. 160, 135, and 110 mg/g-adsorbent, respectively. However, these adsorbents suffer from a rapid decline in adsorption capacities with moderate increases in temperature despite their high CO<sub>2</sub> adsorption capacities at room temperature. In addition, their selectivity to CO<sub>2</sub> in the presence of other gases such as in N<sub>2</sub> is low. High energy input required to regenerate the adsorbent is also a serious drawback.

Recently, a new porous hybrid material, MOF-177, has generated some attention [18] due to its huge CO<sub>2</sub> gas storage capacity at 30 atm and room temperature conditions, but no selectivity or stability data were reported. It also remains to be seen how the material can be applicable in relation to practical CO<sub>2</sub> capture processes.

A mesoporous silica, MCM-41, was discovered in 1992 by Mobil researchers [19,20] and has been extensively studied by others [21–28]. This material appears to be an excellent starting point for the synthesis of silica with large pore volume and pore size. Various surface functionalizations of mesoporous silica materials with several different types of organosilane groups for application in adsorption and catalysis have recently been reported [29–38]. Efforts have also been exerted to use mesoporous silica materials functionalized with various amine groups to mimic liquid phase sorption of CO<sub>2</sub>. Among these, amine-grafted or coated MCM-41 or MCM-48 was found to be an effective adsorbent for CO<sub>2</sub> at moderate temperatures. Initially, Leal et al. [29] tested silica gel grafted with a 3-aminopropyl group and reported a CO<sub>2</sub> adsorption capacity of 19.6 mg/g of adsorbent at STP (0 °C, 1 atm). Huang and Yang [30] studied an amine-grafted MCM-48 and reported that the amount of CO<sub>2</sub> adsorbed reached 98.2 mg/g of adsorbent at 1 atm and 25 °C. Harlick and Sayari [1,36,37] extended the work in this area and exploited the high pore volume and diameter of a pore-expanded MCM-41 silica to introduce a larger quantity of 3-[2-(2-aminoethylamino)ethylamino] trimethoxysilane by a coating method after pre-adsorption with water. They reported an adsorption capacity as high as 120 mg/g-adsorbent at 25 °C and 1 atm total pressure.

Xu et al. [31,32] impregnated a mesoporous silica MCM-41 with polyethylenimine (PEI) dissolved in methanol and achieved a sorption capacity of 115 mg/g-adsorbent at 75 °C with high selectivity to CO<sub>2</sub> using a composite material. This attempt appears to be more practical in terms of cost and ease of preparing the material in comparison with the multi-step post-synthetic grafting procedure necessary for amine-grafted mesoporous silica materials. Similarly, Yue et al. [39] claimed high CO<sub>2</sub> adsorption capacity (173 mg/g of adsorbent at 75 °C) using the SBA-15 impregnated with tetraethylenepentamine.

MCM-41 with ca. 3 nm diameter in a 1D pore arrangement has been mostly utilized as a support material for either amine grafting or PEI impregnation for CO<sub>2</sub> adsorption. It is thought that the textural properties of mesoporous silica materials can influence the adsorption performances of CO<sub>2</sub> in that a mesoporous silica with larger pores can enhance the sorption capacity of the material by accommodating a larger amount of PEI to capture CO<sub>2</sub>. At the same time, a mesoporous silica with 3D channel arrangement can promote more efficient diffusion of CO<sub>2</sub> to the adsorption sites.

In this work, we have prepared a wide range of mesoporous silica support materials with different textural properties and impregnated them with PEI to investigate the effect of pore size and arrangement of the support materials on the CO<sub>2</sub> adsorption capacity and adsorption-desorption rate.

## 2. Experimental

### 2.1. Synthesis of mesoporous silica materials

Mesoporous silica materials, MCM-41, MCM-48, KIT-6, SBA-15, and SBA-16, were prepared for use as a support material for PEI impregnation. MCM-41 was synthesized using cetyltrimethylammonium bromide (CTMABr, Aldrich) as a templating agent. NaOH (1.0 g) was first dissolved in 25 g of distilled water. A silicate solution was prepared by adding 7 g of colloidal silica HS-40 (Aldrich, 40 wt%) to the NaOH solution under stirring at 50 °C. CTMABr solution prepared by dissolving 4.6 g of CTMABr in 25 g of distilled water was then added dropwise to the silicate solution under stirring at room temperature. The pH of the solution was adjusted to 11 using 1 N of acetic acid (Aldrich). After being stirred continuously for an additional 6 h at room temperature, the gel mixture was transferred to a polypropylene bottle and statically heated at 100 °C for 72 h. The solid product obtained was recovered by filtration, washed with distilled water, and dried at 50 °C for 24 h. The as-synthesized sample was calcined in air at 550 °C for 5 h [19–22].

SBA-15 was synthesized using a tri-block copolymer, EO<sub>20</sub>-PO<sub>70</sub>-EO<sub>20</sub> (Pluronic P123, BASF). For a typical synthesis, 10 g of P123 was added to 380 ml of 1.6 M HCl (37%, Aldrich). After stirring for 1 h, 21.3 g of TEOS (98%, Aldrich) was added to the solution with vigorous

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