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CO_2 adsorption performance of different amine-based siliceous MCM-41 materials

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Abstract

A series of amine-based adsorbents were synthesized using siliceous MCM-41 individually impregnated with four different amines (ethylenediamine (EDA), diethylenetriamine (DETA), tetraethylenepentamine (TEPA) and pentaethylenehexamine (PEHA)) to study the effect of amine chain length and loading weight on their CO_2 adsorption performances in detail. The adsorbents were characterized by FT-IR, elemental analysis, and thermo-gravimetric analysis to confirm their structure properties. Thermo-gravimetric analysis was also used to evaluate the CO_2 adsorption performance of adsorbents. Longer chain amine-based materials can achieve higher amine loadings and show better thermal stability. The CO_2 adsorption capacities at different temperatures indicate that the CO_2 adsorption is thermodynamically controlled over EDA-MCM41 and DETA-MCM41, while the adsorption over TEPA-MCM41 and PEHA-MCM41 is under kinetic control at low temperature. The chain length of amines affects the CO_2 adsorption performance and the adsorption mechanism significantly. The results also indicate that CO_2 adsorption capacity can be enhanced despite of high operation temperatures, if appropriate amines (TEPA and PEHA) are applied. However, adsorbents with short chain amine exhibit higher adsorption and desorption rates due to the collaborative effect of rapid reaction mechanisms of primary amines and less diffusion resistance of shorter chain length amines.

Key words

amine-based MCM-41; CO_2 adsorption; chain length; adsorption mechanism; diffusion mechanism

1. Introduction

In the next few decades, fossil fuels will remain a major source of energy for years to come. CO_2 emissions from fossil fuel combustion have attracted more concern due to its important impact on global-warming [1]. For this reason the development of an effective means to capture CO_2 from flue gases is essential to cope with the worldwide demand of CO_2 reduction. Various methods have been proposed to capture CO_2, including cryogenic processes [2], absorption by aqueous solvents [3,4], membrane separation [5], and alkylamine solvents [6]. Ordered mesoporous silica, such as MCM-series [7,8], SBA-series [9,10] and HMS [11], possesses high surface areas, large and uniform pores, and tunable pore sizes as well as a large number of surface sites. These materials have been proven to be promising materials as catalysts and adsorbents. However, when they are used as adsorbents, physical adsorption tends to be insignificant under high temperature, which is the major drawback for CO_2 adsorption from flue gases. Because the amine groups can potentially enhance the CO_2-adsorbents interaction with high CO_2/N_2 selectivity [12] and can be operated at relatively high temperatures, a number of amine types have been investigated for impregnating or grafting them onto mesoporous silica materials to capture CO_2, due to the great potentials to create highly efficient materials as CO_2 adsorbents.

Many researchers approved that the CO_2 adsorption capacity was one of most critical factors to consider when measuring the performance of amine-based adsorbents [13,14]. The majority of published papers focused on the effect of amine groups on the CO_2 adsorption within the amine-loaded silica adsorbents. Recently, Hiyoshi et al. [15] and Knowles et al. [16] respectively used SBA-15 and HMS as substrates to synthesize amine-based adsorbents, including aminopropylsilyl-(AP-), ethylenediamine[propyl(silyl)]-(ED-) and diethylenetriamine[propyl(silyl)]-(DT-). Their results identified that the CO_2 adsorption capacity was a function of the amine content in the amine-based adsorbents, and

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the DT-functionalized material had a higher CO_2 adsorption capacity but lower amine efficiency than AP- or ED-functionalized materials. Hiyoshi et al. [9] also studied SBA-15 grafted with aminopropyltriethoxysilane (APS), N-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AEAPS), and (3-trimetho-xysilylpropyl)diethylenetriamine (TA) separately, and found that the capacities of different amino silanes at the same surface density of amine were in the increasing order of APS>AEAPS>TA. Ko et al. [17] used (3-aminopropyl)trimethoxysilane (APTMS), [3-(methylamino)propyl]trimethoxysilane (MAPTMS), and [3-(diethyl-amino) propyl]trimethoxysilane (DEAPTMS) as amine source to explore the effect of primary, secondary, and tertiary amino silica adsorbents on CO_2 adsorption. The results confirmed that the adsorbed CO_2 was easily desorbed from the adsorbent in the order of tertiary>secondary>primary amino-adsorbents, while the adsorption capacity and the bonding-affinity increased in the reverse order. Furthermore, Serna-Guerrero et al. [18] also found that the increase of the CO_2 adsorption capacity correlated with the amine content. Using grafting method, a significant part of the pore volume remains unfilled despite of high amine loadings. In contrast, using impregnation, the extent of the amine functionalization depends on the total pore volume. Thus, in the latter case the amine may completely fill the pores [19]. However, the weight percentage of amines does not coincide with a corresponding benefit in other important parameters, such as thermal stability and/or adsorption rate, which may result from clogging or collapsing. Consequently, appropriate amine loading and amine chain length should be exercised and chosen when impregnating these amine groups into the substrates so as to make sure that the amine groups disperse evenly [20]. As mentioned above, many authors have suggested the potential importance of amine types and amine loading towards CO_2 adsorption capacity. Nevertheless, few studies investigated the adsorption mechanisms of different amine types related to amine chain length. Additionally, the CO_2 adsorption capacity is still far from the desired targets.

In this work, siliceous MCM-41 is chosen as the substrate. Although the scale-up of MCM-41 production is not available now in terms of its present cost, it is still a material of great potential due to its high surface area and regular periodic framework structure, as well as rapid gas diffusion rate. Moreover, the synthesis technology of MCM-41 is quite mature as well [7]. Four amines with gradual increasing chain length are used as the amine base to synthesis MCM-41 loaded amine with different amine loading. CO_2 adsorption capacity, adsorption rate and thermal stability of these amine-based adsorbents are studied. The work aims to discuss the effect of amine chain length on the CO_2 adsorption performance of amine-based MCM-41 and to explore the guiding principle for synthesizing appropriate adsorbents with higher CO_2 adsorption capacity which can be operated at higher temperature. The present study also contributes a fundamental understanding of the adsorption mechanisms and how the structure of amine groups affects the adsorption performance, which will further improve the CO_2 adsorption capabilities.

2. Experimental

2.1. Synthesis of amine-based MCM-41 adsorbents

Ethylenediamine (EDA), diethylenetriamin (DETA), tetraethylenepentamine(TEPA) and pentaethylenehexamine (PEHA) were used as the organic amine base in this study due to their gradual increasing amine chain lengths as listed in Table 1. Siliceous MCM-41 was prepared in the presence of cetyltrimethylammonium bromide (CTAB) and tetraethylorthosilicate (TEOS) according to the procedure reported in Ref. [21]. All of the amine-loaded materials were prepared by impregnation method. Typically, a desired amount of amine (EDA, DETA, TEPA, and PEHA) was dissolved in 10 mL dry ethanol. The mixture was stirred to make the amine be well dissolved, and then 0.5 g MCM-41 was added. The obtained slurry was continuously stirred at room temperature until sufficiently blended and then sealed to stand for 12 h in air, followed by drying for 8 h at 80 °C in a drying oven considering the boiling point of EDA of 116 °C. Hereafter, the amine-based samples with different amine loading were denoted as 10 wt%, 20 wt%, 40 wt%, 45 wt%, and 50 wt% EDA-MCM41, DETA-MCM41, TEPA-MCM41, and PEHA-MCM41, respectively.

Table 1. Four amines with different chain lengths used as amine sources in this work

Amine	Molecular weight (g/mol)	Density (g/mL)	Formula
Ethylenediamine (EDA)	60.10	0.90	$H_2NCH_2CH_2NH_2$
Diethylenetriamine (DETA)	103.17	0.96	$H_2NCH_2CH_2NHCH_2CH_2NH_2$
Tetraethylenepentamine (TEPA)	189.31	0.95	$NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$
Pentaethylenehexamine (PEHA)	232.30	1.00	$H_2N(C_2H_4NH)_5H$

2.2. Characterization

Elemental analysis was carried out using vario MACRO cube elemental analyzer (Elementar, German) to determine C, H and N contents in the samples. Infrared spectra of MCM-41 and amine-based MCM-41 were recorded in the 4000−450 cm^{-1} region using Spectrum100FT-IR (PerkinElmer, USA).

Pore diameters and surface areas of the samples were evaluated via N_2 physical adsorption analysis using ASAP2020 (Micromeritics, USA). Each sample was degassed at 350 °C, 1.33 Pa under nitrogen flow for 5 h prior to