



Dynamic performance of CO₂ adsorption with tetraethylenepentamine-loaded KIT-6

Yamin Liu, Jingjin Shi, Jie Chen, Qing Ye, Hua Pan, Zhenhua Shao, Yao Shi *

Institute of Industrial Ecology and Environment, Department of Chemical and Biological Engineering, Zhejiang University (Yuquan Campus), Hangzhou 310027, PR China

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ABSTRACT

A promising adsorbent for CO₂ removal from flue gas was prepared by introducing tetraethylenepentamine (TEPA) into KIT-6 type mesoporous silica using post-synthetic impregnation. The as-prepared adsorbents were characterized by X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), nitrogen adsorption/desorption as well as adsorption-column-breakthrough measurements. Surface area, pore size and pore volume of TEPA-loaded KIT-6 adsorbent decrease with the increasing of TEPA loading, while its fundamental pore structure is unchanged. The dynamic adsorption capacity increases from 1.5 mmol/g-adsorbent to 2.9 mmol/g-adsorbent when the amount of loaded TEPA increases from 10 wt.% to 50 wt.% at 333 K. The net adsorption capacity is about 72% of dynamic adsorption capacity. Regarding the regeneration performance of CO₂ adsorbent, the suitable desorption temperature is nearly 373 K. The dynamic adsorption capacity drops slightly (about 5%) during forty cycles of adsorption/desorption. The adsorbent of KIT-6 modified by TEPA exhibits excellent CO₂ adsorption/desorption performance.

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1. Introduction

Extensive efforts have been devoted in reducing greenhouse gas emissions, especially for CO₂ capture and storage (CCS) [1,2]. Up to date, viable separation methods, including absorption [3,4], adsorption [5–9] and membranes [10] technology have been widely developed for capturing CO₂ from flue gas. The conventional CO₂ removal method is liquid amine scrubbing technology [11]. There are some limitations for the liquid-phase absorption, such as large amounts of energy consumption [12], corrosive and toxic nature [13]. Inspired by this technology, a number of research groups have developed amine functioned solid adsorbents for CO₂ capture [7,8,14–17]. Adsorption approach is one of the most promising methods due to high selectivity and low energy penalties.

Adsorbents can be classified into two groups: physisorbents and chemisorbents [18]. Physisorbents (such as activated carbon [19] and zeolites [20]) act as molecular sieves and adsorb CO₂ onto their surfaces. They are non-toxic, high surface area, and relatively inexpensive to manufacture. However, their selectivity to CO₂ in the presence of other gases (N₂, H₂O, etc.) is still low. The chemisorbents can chemically react with CO₂. Most of them are amine functionalized supported materials [18].

Supports of adsorbents include silica gels [21], active carbon [22], molecular sieves [15] and polymers [23]. Ordered mesoporous silica, such as MCM-series, SBA-series and KIT-series, are ideal solid supports for their large and uniform pores, tunable pore sizes,

high surface area and a large number of highly dispersed active sites (the hydroxyl groups) on the pore walls and surfaces. The modification of mesoporous silica has been widely investigated recently. Huang et al. [24] found that the amount of CO₂ adsorbed was 2.2 mmol/g (amine-grafted MCM-48) under 101.325 kPa at 298 K. Hiyoshi et al. [7] prepared CO₂ adsorbents by grafting various aminosilanes on mesoporous silica SBA-15. They reported that the adsorption capacity reached 1.8 mmol/g-adsorbent under 15 kPa CO₂ at 333 K, and found that the efficiency of amine increased with increasing surface density of amine. In our previous work [9,25], CO₂ adsorption of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane functionalized SBA-16 was studied. The adsorption capacity was 0.727 mmol/g-adsorbent under 101.325 kPa at 333 K, the adsorbent showed high hydrothermal stability.

Compared with grafting procedure, impregnation process appears to be more feasible in terms of low cost and convenient preparation. And a larger amount of amine can be loaded on the support by impregnation. The adsorption capacity of adsorbents prepared by impregnation chiefly depends on the amount of amine loadings and the distribution of the amine groups. More amine loadings bring larger CO₂ adsorption capacity. However, not all the loaded amine groups can interact with CO₂ due to conglomerate of amine molecules in the host [26]. Inner amine groups of the conglomerate cannot contact with CO₂. Amine sites on the surface of the conglomerate cannot totally interact with CO₂ for the reason of steric hindrance.

Recently, CO₂ adsorbents (amine-mesoporous silica) prepared by impregnation have attracted much attention [8,27–30]. Yue et al. [8] obtained a high CO₂ adsorption capacity of

* Corresponding author. Tel.: +86 571 88273591; fax: +86 571 88273693.
E-mail address: shiyao@zju.edu.cn (Y. Shi).

3.36 mmol/g-adsorbent using tetraethylenepentamine (TEPA) loaded SBA-15. Xu et al. [27] studied the polyethyleneimine (PEI) modified MCM-41 silica by impregnation. An adsorption capacity of 2.6 mmol/g-adsorbent was obtained at 348 K. Son et al. [28] impregnated a series of silica materials (MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6) with 50 wt.% PEI in methanol. The PEI loaded KIT-6 showed the highest CO₂ adsorption capacity of 3.1 mmol/g-adsorbent. Su et al. [30] prepared TEPA modified Y-type zeolite. An adsorption capacity of 2.56 mmol/g-adsorbent was obtained at 333 K. To our knowledge, the adsorbent's adsorption capacity and its hydrothermal stability under dynamic conditions were rarely reported.

In this work, a mesoporous silica KIT-6 was impregnated with TEPA dissolved in ethanol. KIT-6 was chosen as a support due to the good accessibility for modification and adsorption. TEPA was selected for the low cost, low toxicity and high concentration of amine groups for interacting with CO₂. Characteristics of functionalized KIT-6 and dynamic adsorption/desorption performance were investigated.

2. Experimental

2.1. Preparation of KIT-6 support

KIT-6 support was synthesized using tri-block copolymer, EO₂₀-PO₇₀-EO₂₀ (AR, Pluronic P123, Aldrich) with an average molecular weight of 5800 as a surfactant, *n*-butanol (AR, Hangzhou Chem. Reagent Co.) as a structure-directing mixture and TEOS (tech, Aldrich) as silica source. The mole ratio TEOS:P123:HCl:H₂O:*n*-butanol of the mixture was 1:0.017:1.83:195:1.31. In a typical process, 4.0 g P123 was added in a mixture of 144 g distilled water and 7.9 g 35 wt.% HCl (AR, Hangzhou Chem. Reagent Co.), then the mixture was stirred at 313 K. After the P123 totally dissolved in the solution, 4.0 g BuOH was added. The mixture continued stirring at 313 K for 1 h. Then 8.6 g TEOS was added to the homogeneous clear solution. This mixture was left under vigorous stirring at 313 K for 24 h. Later, the mixture was aged at 373 K for 24 h under static conditions. Finally, the white precipitation product was hot-filtered without washing and dried in air at 373 K for 24 h. Surfactant-free KIT-6 was obtained after calcination at 823 K in air. All chemicals were used without further purification.

2.2. Synthesis of TEPA-loaded KIT-6 silica

TEPA (purity: >95%, Aldrich) was introduced into KIT-6 silica through wet impregnation. The desired amount of TEPA was dissolved in 50 g ethanol (AR, Hangzhou Chem. Reagent Co.) under stirring for 40 min at room temperature, and then 1 g KIT-6 support was added. After stirring and refluxing for 4 h, the mixture was evaporated at 353 K. Subsequently, the samples were dried in air for 1 h at 373 K. These composites were denoted as KIT-6-*n*, where *n* represents the weight percentage of TEPA in the composites. For instance, KIT-6 silica was loaded with 40 wt.% TEPA, the obtained sample was named as KIT-6-40, which contained 40 wt.% TEPA and 60 wt.% KIT-6 support.

2.3. Characterization of samples

X-ray diffraction (XRD) measurements were performed on a Rigaku powder diffractometer (Rigaku, Japan) with Cu K α radiation. The tube voltage was 45 kV, and the current was 40 mA. The XRD diffraction patterns were taken in the 2θ range of 0.5–10° at a scan speed of 2°/min.

Nitrogen adsorption/desorption was measured by a BELSORP instrument (BELSORP-mini II Inc., Japan). KIT-6 sample was de-

gassed at 573 K under nitrogen flow for 8 h and TEPA-loaded samples were out-gassed at 373 K for 24 h prior to measurement. Nitrogen adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K). Surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were determined by Barrett–Joyner–Halenda (BJH) method. Total pore volume was calculated from the amount of adsorbed N₂ at $P/P_0 = 0.99$.

Thermal gravimetric analysis (TGA) was carried out with a TGA (SDT Q600, TA Instruments) under dynamic N₂ atmosphere from 313 K to 573 K with a heating rate of 10 K/min.

2.4. Adsorption of carbon dioxide

To obtain dynamic adsorption capacity and breakthrough curve, the CO₂ adsorption experiments were performed in a tubular flow adsorber (quartz glass column) inside a tubular furnace. The tubular flow adsorber is 14 cm in length and 1 cm inner diameter. Inlet gas was a mixture of CO₂ (99.99%) and N₂ (99.99%) at predetermined composition with a CO₂ mole fraction of 10% at atmospheric pressure. The concentration of CO₂ was measured by a gas chromatograph (GC) connected on line to the adsorber outlet, by injecting successive pulses of gas samples from the reactor exit stream. In a typical experiment, adsorbents were treated under a nitrogen flow of 100 cm³/min at 383 K for 1 h, and then cooled to 333 K. The nitrogen flow was then switched to the CO₂-containing mixture at a flow rate of 80 cm³/min. Carbon dioxide mole fraction was kept at 10% at atmospheric pressure.

The dynamic adsorption capacity is calculated from the breakthrough curve using Eq. (1):

$$Q_{\text{ads}} = \frac{FC_{\text{in}}t_{\text{st}}}{M} \quad (1)$$

where Q_{ads} is the dynamic adsorption capacity, cm³/g-adsorbent or mmol/g-adsorbent; F is total flow rate, cm³/min or mmol/min; C_{in} is the concentration of CO₂ entering the column, vol.% or mmol%; M is the mass of adsorbent loaded in the column, g; and t_{st} is the stoichiometric time corresponding to CO₂ stoichiometric adsorption capacity, min. The stoichiometric adsorption capacity can be shown to be proportional to the area between the breakthrough curve and a line at $C_{\text{ou}}/C_{\text{in}} = 1.0$. Note, t_{st} can be estimated from the breakthrough profile according to Eq. (2) [32]:

$$t_{\text{st}} = \int_0^t \left(1 - \frac{C_{\text{ou}}}{C_{\text{in}}}\right) dt \quad (2)$$

where C_{ou} is CO₂ concentration of mixture gas downstream the adsorber column, vol.% or mmol%; t is the time at which the C_{ou} reaches its maximum permissible level, min.

The net dynamic adsorption capacity Q_{n} is defined as CO₂ adsorption quantity before CO₂ is detected at the outlet of the adsorber, cm³/g-adsorbent or mmol/g-adsorbent.

The gravimetric equilibrium capacity Q_{eq} is obtained by TGA, cm³/g-adsorbent or mmol/g-adsorbent. In a typical experiment, 10 mg samples were loaded into a 0.05 cm³ platinum sample pan. Each sample was first regenerated (heated at 383 K) in the flow of N₂ (120 cm³/min) before adsorption, then cooled to 333 K prior to exposure to the CO₂/N₂ mixture (10 vol.%) for about 50 min. The adsorption capacity is calculated based on TGA weight gain and the dry mass of the material versus time.

2.5. Desorption of carbon dioxide

All experiments of CO₂ desorption from adsorbents were performed after CO₂ was adsorbed completely. The concentration of CO₂ in outlet gas was measured by GC on line. The desorption procedure was carried out by a temperature program desorption

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