



Development of efficient amine-modified mesoporous silica SBA-15 for CO₂ capture

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ARTICLE INFO

Article history:

Received 1 February 2013

Received in revised form 6 June 2013

Accepted 9 June 2013

Available online 18 June 2013

Keywords:

A. Nanostructures

A. Structural materials

C. Infrared spectroscopy

C. Thermogravimetric analysis (TGA)

ABSTRACT

A novel CO₂ sorbent was prepared by impregnating mesoporous silica, SBA-15, with acrylonitrile (AN)-modified tetraethylenepentamine (TEPA) in order to increase CO₂ adsorption capacity and improve cycling stability. The mesoporous silica with pre- and post-surface modification was investigated by X-ray diffraction characterization (XRD), N₂ adsorption–desorption test (N₂-BET), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The adsorption/desorption performance of S-TN (TN: AN modified TEPA) and S-TEPA was studied by dynamic adsorption. Test results showed that the solid base-impregnated SBA-15 demonstrated high CO₂ adsorption capacity (180.1 mg g⁻¹-adsorbent for 70% amine loading level). Compared to S-TEPA (24.1% decrease of initial capacity), S-TN with 50% amine loading exhibited improved cycling stability, 99.9% activity reserved (from initial 153.0 mg g⁻¹ to 151.3 mg g⁻¹) after 12 cycles of adsorption/desorption at 100 °C. A mechanism of molecular structure of the loaded amine was attributed to the improved performance.

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1. Introduction

Anthropogenic CO₂ emissions may influence the troposphere and the atmosphere at nearly all altitudes between the ground and the upper thermosphere, thus affect not only life on earth, but also space-based technological systems [1]. Carbon dioxide capture and storage (CCS) has been seen as a major solution for reducing global emissions of CO₂ [2]. Various methods proposed for capturing CO₂ from the atmosphere include adsorption, absorption, membrane separation and biotechnology [3,4]. Among these methods, organically functionalized porous adsorbents, such as mesoporous silica, have attracted considerable attention because of their high efficiency and excellent selectivity in CO₂ capture from gas mixtures [5,6]. Chemically grafting organosilanes [7] and physically impregnating amines [8] are the main strategies developed on mesoporous silica functionalization. The later impregnation protocol has gained wide application due to its simplicity and high amine loading yield. However, some amines such as poly(ethylenimine) (PEI) [8,9], tetraethylenepentamine (TEPA) [10] and diethanolamine (DEA) [11] were unstable and their adsorption capacity decreased with cycle numbers, which was mainly due to the molecular structure of the amines. Yan et al. [12] reported that MCF (a)/PEI-60% showed a maximum CO₂ adsorption capacity of

198 mg g⁻¹ sorbent at 70 °C. Similarly, although multiamine could effectively improve the CO₂ adsorption capacity, stability issue has been encountered. TEPA-impregnated MCM-41 dropped its adsorption capacity from 200 to 183 mg g⁻¹ after six cycles, according to Yue's research [13]. The CO₂ adsorption capacity of SBA-15-PEI (50) remained only about 93% of its original value during only 4 cycles of regeneration–reuse [14]. By immobilizing a secondary amine AN-MEA (AN and monoethanolamine adduct of Michael addition) within the pores of polymeric supports, Filburn et al. [15] achieved an increase in CO₂ removal by nearly a factor of 2, compared to the original primary amine MEA. The relatively high volatility and liability to oxidation of the primary amine were considered to be drawbacks in terms of sorbent stability.

It should be pointed out that the initial adsorption capacity of M₄-TEPA-50 (TEPA-impregnated disordered mesoporous silica M₄ with 50 wt.% amine loading) was also high (193.8 mg g⁻¹) in our previous investigation [16], but the value sharply decreased 48.2% after 5 cycles of regeneration, and the sample gradually became yellow. M₄-TM-50, an acrylamidation product of TEPA (TM) modified M₄, significantly improved its stability performance, by less than 1% of initial capacity loss after 12 cycles of adsorption/desorption. These results suggest that modified amines could potentially be used for the applications of CO₂ removal from terrestrial flue gas.

The aim of this work is to investigate the CO₂ adsorption capacity and the stability of mesoporous silica SBA-15 impregnated with AN-modified TEPA, in comparison with S-TEPA. By

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converting the primary amine to secondary amine, the impacts of molecular structure change on amine loading, adsorption temperature, and adsorption/desorption cycles were evaluated to characterize the adsorbent and to ascertain the adsorption mechanism.

2. Experimental

2.1. Chemicals

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) Pluronic P123 (PEO₂₀PPO₇₀–PEO₂₀, Mn = 5800) were purchased from Sigma–Aldrich and used as received. Tetraethyl orthosilicate (TEOS, 98%), tetraethylenepentamine (TEPA), acrylonitrile (AN), methanol (MeOH), HCl and NaOH were obtained from Sinopharm.

2.2. Preparation of the adsorbents

2.2.1. Synthesis of AN-modified TEPA

AN-modified TEPA was synthesized by Michael addition, which was illustrated in Scheme 1. The reaction was carried out in a thermostatic three-necked round-bottom flask equipped with a mechanic stirrer and a dropping funnel. Following the passing of nitrogen for 30 s, acrylonitrile (2 equiv., 25% aqueous solution) was added dropwise to TEPA solution in ice bath. Then the mixture was heated up to 50 °C and kept for 1 h. Water was eliminated from the mixture by vacuum. The TEPA–AN (TN) product obtained was pale yellow viscous liquid and totally water-soluble.

2.2.2. Preparation of mesoporous SBA-15

The SBA-15 was prepared according to the hydrothermal method by using P123 as a structure directing agent and TEOS as a silica source following the literature [17]. Briefly, P123 was dissolved in the mixture of deionized water and 2.0 M HCl under vigorous stirring at 35 °C, then the reaction mixture were formed by adding TEOS to the sample dropwise for 45 min. The molar ratio of the reaction mixture was 1 TEOS: 0.017 P123: 5.88 HCl: 136 H₂O. After stirring for 24 h at the same temperature, the sample was transferred to an autoclave and aged for 24 h at 100 °C. The white gel was isolated by filtration and washed with distilled water and ethanol, and then calcined in air under a thermal ramp of 2 °C/min to 550 °C for 6 h.

2.2.3. Modification of SBA-15 by TN and TEPA

TN was impregnated into SBA-15 by using the following procedure [9]. The required amount of TN was dissolved in methanol before being added to the SBA-15 support. The resulting slurry was continuously stirred at room temperature until the solvent was evaporated, followed by drying at 60 °C under reduced pressure. The obtained adsorbents were designated as S-TN-*n*, where *n* represents the weight percent of TN in the adsorbent. The amounts of added SBA-15, TN and methanol are specified in Table 1. And the samples of S-TEPA-*n* were prepared in the same way.

2.3. Characterization of adsorbents

The structures of the mesoporous materials were obtained by X-ray diffraction (XRD) on a Philips X'Pert PRO SUPER X-ray

Table 1

Amounts of SBA-15, TN and methanol used for preparation of S-TN-*n* samples.

Sample	TN (g)	SBA-15 (g)	MeOH (g)
S-TN-30	0.6	1.4	15
S-TN-40	0.8	1.2	15
S-TN-50	1.0	1.0	15
S-TN-60	1.2	0.8	15
S-TN-70	1.4	0.6	15
S-TN-80	1.6	0.4	15

diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The N₂ adsorption/desorption isotherms were collected at 77 K using a Micromeritics TriStar 3000 Porosimeter. The adsorbent was degassed prior to each measurement at 100 °C in a high vacuum for 3 h. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were derived from the desorption branch of isotherms based on the Barrett–Joyner–Halenda (BJH) method. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of $P/P_0 = 0.99$. Transmission electron microscopy (TEM) measurements were taken on a JEOL JEM-2100F 200 kV. Fourier transform infrared spectra (FTIR) were obtained using a Nicolet MAGNA 750 Spectrometer by measuring the absorbance of the KBr pellet containing 1–2 wt.% of sample. Thermal, chemical, and physical properties of the S-TN-50 were characterized by thermal gravimetric analysis (TGA) performed on a Perkin-Elmer-TGA7 analyzer.

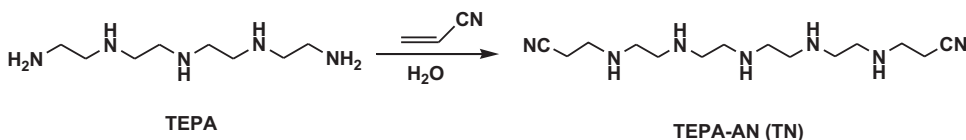
2.4. CO₂ adsorption/desorption measurement

The CO₂ adsorption/desorption measurement for S-TN-*n* samples were performed on an assembled flow adsorber (quartz-lined stainless steel U-tube with inner diameter of 20 mm) operated at atmospheric pressure [16,18]. 2 g of sample was placed at the bottom of the u-pipe, with one end connected to the gas cartridge and another linked to a portable IR gas analyzer (GXH-3011N) equipped with an online computer. The initial activation of samples was carried out at 100 °C for 2 h in N₂ atmosphere at the rate of 80 mL min⁻¹ to eliminate the existence of water and CO₂. The process of adsorption was operated using highly pure (99.999%) CO₂ at a flow rate of 80 mL min⁻¹, while the desorption run was conducted at 100 °C in N₂ stream at constant pressure. Adsorption capacity in mg-adsorbate/g-adsorbent and desorption capacity in weight change percentage were used to evaluate their adsorption/desorption performance.

3. Results and discussion

3.1. TN impregnated into SBA-15 substrate

Small angle XRD diffractograms for pure SBA-15 and TN-modified SBA-15 samples are shown in Fig. 1. The pattern of SBA-15 silica diffractogram appeared as a predominant signal corresponding to the (1 0 0) crystal face at $2\theta = 0.9^\circ$ and two small diffraction peaks at higher angles. The pattern of TN-impregnated SBA-15 is approximately the same as SBA-15 with decreased peak intensity and slightly higher angle-shifted peak



Scheme 1. Synthesis of TEPA-AN (TN).

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