



Titanium-incorporated organic–inorganic hybrid adsorbent for improved CO₂ adsorption performance



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ABSTRACT

The CO₂ adsorption performance of acrylonitrile (AN)–tetraethylenepentamine (TEPA) adduct (hereafter referred to as TN) impregnated adsorbent was greatly enhanced by introduction of Titanium atom into the silica matrix. The adsorbents were characterized by X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption/desorption, UV–vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy. The adsorption experiments together with the physicochemical characterization demonstrated that these adsorbents containing an optimal amount of Titanium (Ti/Si ≈ 0.1) remarkably reinforced the CO₂ adsorption capacity and recycling stability. The highest CO₂ uptakes reached 4.65 and 1.80 mmol CO₂/g adsorbent at 25 °C under 90% CO₂ (CO₂/N₂, 90:10 V/V) and 1% CO₂ (CO₂/N₂, 1:99 V/V) conditions for sample Ti(0.1)-DMS-TN, respectively. Repeated adsorption/desorption cycles revealed that the Ti-incorporated adsorbent showed only a tiny decrease in adsorption capacity (1.778 mmol CO₂/g adsorbent after 15 cycles, decreased by 0.95%), significantly enhanced the adsorbent recycling stability.

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1. Introduction

Carbon dioxide capture and storage (CCS) by advanced materials and technologies is commonly seen as a major solution to global warming and ocean acidification problems [1]. Capturing CO₂ from the atmosphere or flue gas stream can be achieved by several approaches, including cryogenic distillation, membrane purification, absorption and adsorption [2,3]. Among them, adsorption process using a variety of different types of solid materials has many potential advantages as it is tunable, reusable and cost-effective [4].

In developing the solid CO₂ adsorbents, three major areas of concern where researchers focus on their efforts are: (1) the CO₂ capture capacity, (2) energy consumption in desorption process, (3) the recycling stability. Although the first one seems the most important, but no CO₂ adsorbent can be regarded as being interesting without being repeatedly regenerated at the lowest temperature possible. Apparently, recycling stability is also a big issue that needs to be addressed for long term and economical application of the adsorbent. To enhance the CO₂ capture capacity, porous solid supports such as activated carbons, carbon nanotubes, metal oxides, mesoporous molecular sieves were commonly

modified with small molecule amines or aminopolymers. Among them, silica has been used as the support material in the vast majority of preparations of the amine-modified adsorbents [5–7]. This solid amine technology integrates the advantages of absorption and adsorption. The CO₂ capture mechanism involves the chemical reaction through carbamate formation and physical interactions with silanol [8]. Therefore, the CO₂ adsorption performance can be improved by altering the nature of the amine groups [9,10], adjusting the porosity of the silicate support [11,12] and changing the silica surface characteristics [13,14]. Recently, the introduction of heteroatom Zr on the surface of matrix has been reported to provide effective cooperation between the amines and the solid surface [15,16].

Inspired from the above basis, the aim of this work was to combine the metal incorporation, the base amine modification and the structurally disordered porous silica support to make solid CO₂ capture materials that show improved CO₂ adsorption capacity and durability. The novel aspect of this work is that this is the first report that uses Ti in preparation of the organic base-pregnant CO₂ adsorbents. TN (Michael addition adduct of AN and TEPA) was chosen as the amine source because of its high amine density and chemical durability due to modified amine structure. The results demonstrated a stabilizing effect of amphoteric Ti sites that enhanced the CO₂ adsorbent capacity in diluted gases, and stability over continued recycling.

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2. Experimental

2.1. Materials

Titanium (IV) isopropoxide ($\text{Ti}(i\text{-PrO})_4$, 97%) was purchased from Sigma–Aldrich. TEPA was obtained from TCI Shanghai. Tetraethyl orthosilicate (TEOS, AR), cetyltrimethyl ammonium bromide (CTAB, AR) and ethanol (EtOH, AR) were purchased from Sinopharm. All of the reagents were used as received without further purification. Siliceous material DMS and amine TN were prepared similar to the procedure described in our previous reports [17].

2.2. Adsorbents preparation

Ti-modified DMS supports were prepared by chemical grafting. $\text{Ti}(i\text{-PrO})_4$ was used as titanium sources and absolute ethanol as the solvent. In the grafting procedure, calcined DMS material was slurried in ethanol. Then, different amounts of the $\text{Ti}(i\text{-PrO})_4$ were dissolved and thoroughly mixed in ethanol and added to the suspensions. After stirring for 8 h at 35 °C, the mixture was evaporated under reduced pressure to remove ethanol. Excesses titanium precursor was eliminated by washing with dry ethanol. The filtered solid was placed in the oven and dried overnight at 85 °C. The powder obtained was then ground finely and calcined at 550 °C for 6 h with a heating rate of 3 °C min⁻¹ to give the Ti-modified DMS supports. The materials are denoted as $\text{Ti}(x)$ -DMS, where x represents the atomic ratio of Ti/Si in the sample.

The preparation of TN modified Ti-DMS adsorbent was carried out by using the following procedure. 1 g of TN was added to the suspension of 1 g of $\text{Ti}(x)$ -DMS in 20 mL of absolute ethanol. The resulting slurry was continuously stirred at 35 °C for 3 h, and then the sample was dried at 60 °C under reduced pressure. The theoretical amine loading for the adsorbents was 50%. The obtained adsorbents were designated as $\text{Ti}(x)$ -DMS-TN.

2.3. Characterization of adsorbents

The materials were characterized by means of X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption/desorption, UV–vis spectrophotometer, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. XRF measurements were performed on a PANalytical AXIOS-X Spectrometer and XRD on a Philips X'Pert PRO SUPER X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). TEM measurements were taken on a JEOL JEM-2100F 200 kV. Static N_2 physisorption experiments were performed using a Micromeritics TriStar 3000 Porosimeter. The samples were degassed prior to each measurement at 100 °C in a high vacuum for 3 h. Micropore volume was calculated using the t -method. The surface areas of all materials were obtained applying the method by BET (Brunauer–Emmett–Teller), whereas the pore size was estimated according the method by BJH (Barrett–Joyner–Halenda). The absorbance spectra of the adsorbents were measured by a UV–vis spectrometer (UV-2550, Shimadzu) in a range of 200–500 nm. The structures of materials before and after functionalization were characterized by the FTIR spectra, and obtained using a Nicolet MAGNA 750 spectrometer by measuring the absorbance of the KBr pellet containing 1–2 wt.% of sample. Elemental analysis of the adsorbent for N was performed by using a PerkinElmer 2400 analyzer.

2.4. CO_2 adsorption/desorption measurement

CO_2 adsorption/desorption data were obtained using a quartz-lined stainless steel U-tube reactor with inner diameter of 20 mm.

In a typical experimental sequence, generally dried sorbent of 2 g was placed in the bottom of U-tube operated at atmospheric pressure. An IR gas analyzer (GXH-3011N) linked with an online computer was used to measure the content of CO_2 in the outlet gases during the experiment. The specified sample was dried at 100 °C for 3 h in N_2 stream at a flow rate of 100 mL min⁻¹. The weight loss due to CO_2 and water desorption. The adsorbent was cooled to the setting temperature with the atmosphere of N_2 after pretreatment. Subsequently diluted CO_2 (CO_2/N_2 , 1:99 V/V or 90:10 V/V) was introduced to the assembled adsorber at a flow rate of 80 mL min⁻¹. Almost immediately the CO_2 concentration in the outlet gases fell to 0%. The CO_2 concentration was recorded by computer at the desired time during the process of adsorption. After saturation of the adsorbent, when the CO_2 concentration reached the inlet value (1%), the adsorption was stopped. The sample was regenerated at 100 °C for 1 h in N_2 stream at ambient pressure. The adsorption capacity of CO_2 on an adsorbent (A , mmol g⁻¹) was calculated as

$$A = \frac{1}{2} \sum_{i=1}^{2t} \left(C_0 - \frac{C_i + C_{i+1}}{2} \right) \times \frac{Q}{V_{\text{mol}}} \times \frac{1}{m}$$

where t was the sorption time (min), C_0 and C_i were the concentration of CO_2 (mg L⁻¹) in input gases and desired sample test (taking it once 0.5 min), respectively. And Q was the flow of CO_2 (L min⁻¹); V_{mol} was the molar volume of gases; m was the weight of sorbent (g).

3. Results and discussion

3.1. Characterization of samples

Four Ti-containing DMS samples were prepared by chemical grafting technique. The high-angle powder XRD patterns of prepared materials were tested to confirm the existence of Ti within the DMS matrix (Fig. 1(A)). It is obvious that DMS is a structurally disordered molecular sieve (see Fig. 1(B)) with the single intense peak at about 23.3° (2θ) accompanied by line broadening. For the materials modified by the titanium, the different lines associated with crystalline TiO_2 appeared in the XRD pattern [18]. As expected from the preparation process, a distinct peak at about 25.2° (2θ) and three slightly weak peaks between 35° and 60° for $\text{Ti}(0.2)$ -DMS, and only three weak peaks detected for $\text{Ti}(0.1)$ -DMS, which reveal that the TiO_2 is of anatase structure (JCPDS: 01-083-2243) with no trace of other phases. Note that no

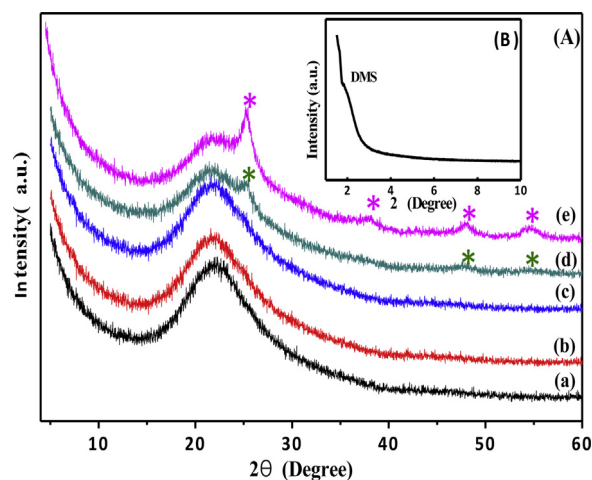


Fig. 1. (A) High-angle powder XRD patterns of DMS (a); $\text{Ti}(0.01)$ -DMS (b); $\text{Ti}(0.02)$ -DMS (c); $\text{Ti}(0.1)$ -DMS (d) and $\text{Ti}(0.2)$ -DMS (e). (B) Low-angle powder XRD patterns of DMS.

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