Nano Energy 25 (2016) 1–8

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

CO_2 removal from flue gas with amine-impregnated titanate nanotubes

Liping Guo [a], Jie Yang [a], Gengshen Hu [b], Xin Hu [a,*], Herbert DaCosta [c], Maohong Fan [d,**]

[a] College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, PR China
[b] Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, PR China
[c] Math, Science, and Engineering Division, Illinois Central College, 1 College Drive, East Peoria, IL 61635, USA
[d] Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

ARTICLE INFO

Article history:
Received 31 December 2015
Received in revised form
16 April 2016
Accepted 20 April 2016
Available online 22 April 2016

Keywords:
CO_2 adsorption
Protoned titanate nanotube
Amines
Flue gas

ABSTRACT

The purpose of this work was to develop a new high-capacity CO_2 sorbent. Protoned titanate nanotube (PTNT) with different porous textures were synthesized by a hydrothermal method and further modified with different types and amounts of amines including triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and polyethyleneimine (PEI) for CO_2 adsorption. Scanning electron microscopy, transmission electron microscopy, nitrogen adsorption, Fourier transform infrared spectroscopy and thermogravimetric analysis were used to characterize PTNT supports or amine composite sorbents. The CO_2 adsorption performances of sorbents were evaluated in a fixed-bed reactor coupled with an online gas chromatograph using a gaseous mixture that resembled realistic flue gas. Experimental results revealed that pore volume rather than surface area of the supports is the dominant factor that determines the CO_2 sorption capacities of the composite sorbents. Furthermore, the CO_2 uptake capacities of the PTNT composite decreased as the size of the impregnated amines increased. The highest CO_2 sorption performance attained with the sorbents is 4.33 mmol/g for a PTNT with 60 wt% TETA loading under simulated flue gas condition. It is also found that enhanced contact between CO_2 and the impregnated amine was obtained when there was a small space left within the pores of the composite sorbent after amine impregnation. Besides high capacity for CO_2 adsorption, the amine-impregnated PTNTs also display positive effect of moisture, good stability and reusability indicating their great potential in CO_2 removal from flue gas.

1. Introduction

CO_2 emission has caused serious environmental concerns, since CO_2 is the major contributor to greenhouse gas and its consequent global warming effect [1]. To mitigate the CO_2 emission, different CO_2 capture techniques have been explored, among which absorption using aqueous amine solution is a state-of-the-art process [2]. This method, however, has high energy penalty, causes corrosion of equipment, in addition to solvent loss, and has high toxicity. In order to circumvent these problems, adsorption with the use of sorbents is proposed as an attractive alternative that can avoid the disadvantages of amine absorption [3–5]. The key of this technology is to find sorbents with superior CO_2 capture capacity under conditions similar to flue gas, which only comprises 10–15% CO_2 with the temperature around 75 °C [6]. Efficient capture of CO_2 under such low CO_2 partial pressures is still a challenge. Presently, most actively researched solid sorbents include porous carbons [7–12], metal oxide [13–15], zeolites [16,17], metal–organic frameworks (MOFs) [18,19], and porous polymer [20]. These materials possess highly developed porosity and can adsorb large amounts of CO_2 by physisorption under low temperature and high pressure. However, these sorbents show rather low CO_2 capacity and selectivity because of the decreased interaction between sorbent and CO_2 under the condition of flue gas. To improve the CO_2 capture capacity, solid-supported amine sorbents have been developed and show great promise [21–27]. In these composite sorbents, the strong interaction between amine and CO_2 molecules results in high CO_2 uptake at the low pressures of CO_2. Of all kinds of porous materials, silica is the most common used substrate. For example MCM-41 [28,29], MCM-48 [30], SBA-15 [31,32], KIT-6 [33], and silica foam [34–36] were explored as supports for development of amine modified composite sorbents. The results of these studies reveal that the pore volume, pore size, and surface area of the supports determine the CO_2 sorption capacity of the composite sorbents [37]. Generally speaking, support with larger pore volume, pore size and surface area can accommodate a larger

* Corresponding author.
** Corresponding author.
E-mail addresses: huxin@zjnu.cn (X. Hu), mfan@uwyo.edu (M. Fan).

http://dx.doi.org/10.1016/j.nanoen.2016.04.038
2211-2855/

amount of amine for CO_2 capture, which is beneficial for the enhancement of CO_2 sorption capacity of the composite sorbents. On the other hand, some works have reported that the surface properties of the supports also played a significant role in creating more effective CO_2 sorbents [14,15,38,39]. For example, protonated titanate nanotube (PTNT) has been used as supports and amine-impregnated protonated titanate nanotube (PTNT) composite sorbents have shown great potential in capture of CO_2 from flue gas i.e. ca. 4 mmol/g CO_2 uptake capacity under conditions of simulated flue gas [40–42]. However, to find the PTNT-based sorbent with higher CO_2 capacity and further understand the CO_2 adsorption mechanism for this system, more systematic studies are needed. With that in mind, this study was designed to enhance our understanding of the characteristics of PTNT-based composite CO_2 sorbents that are synthesized with PTNT having multiple porous structures and various amines, such as triethylenetetramine (TETA), TEPA and polyethyleneimine (PEI). The effects of porous properties of the support and character of the amines on the CO_2 uptake of the resulting composite sorbents are investigated to give more insights in developing new amine/support sorbents for effective CO_2 removal from combustion flue gas.

2. Experimental

2.1. Materials

Anatase Titanium (IV) Oxide (325 mesh) was supplied by Aldrich. This study included the following organic amines: TETA (technical grade), TEPA (technical grade), and PEI (branched, M. W.=600, 99%), supplied by J&K Scientific. NaOH and ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) was supplied by Quzhou reagent Juhua Co., LTD. All experiments used distilled water. All these chemicals were used as obtained, without additional purification.

2.2. Synthesis of protonated titanate nanotube

Three PTNTs with different porous texture were synthesized using a hydrothermal method described elsewhere [41]. Anatase titanium(IV) oxide (2 g) was mixed with 40, 75 or 100 mL 10 mol/L NaOH solution, respectively. After stirring and ultrasonic oscillation, the mixture was transferred to a stainless steel autoclave with Teflon liner and heated at 130 °C for 24 h. After cooling to room temperature, the collected precipitate was firstly washed with 0.1 M HCl solution until the pH value reached about 1.6 and then washed with deionized water to pH=7. The suspension was filtered by suction filtration, and the resulting white solid were put into a vacuum oven at 100 °C overnight. The final product were obtained and designated as T1, T2 and T3, respectively.

2.3. Synthesis of PTNT composite sorbents

Amine functionalized PTNTs were prepared with the wet impregnation method. The typical preparation begins with dissolving the desired amount of amine (TETA, TEPA or PEI) into 10.0 g ethanol, following by stirring for 30 min, and adding 1 g Tx. The slurry that resulted was then stirred and refluxed at 80 °C for 2 h, and dried at 80 °C until it reached complete volatilization of ethanol. The resulting samples were labeled as n-amine/Tx in which n represents the weight percentage of amine in the composites. For example, 50-TETA/T1 represents the sorbent contains 50 wt% TETA and 50 wt% T1 support.

2.4. Characterization

The morphology of PTNT support was obtained by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and a JEOL-2100F transmission electron microscope operated at 200 KV. The pore characteristics of the sorbents were determined with nitrogen adsorption at −196 °C using Beishide 3H-2000PS2 analyzers. The PTNT and amine functionalized composite sorbents were degassed at 150 °C and 80 °C under vacuum at 1×10^{-3} Torr for a period of at least 12 and 4 h, respectively. The surface area was obtained from calculations using the multipoint Brunauer-Emmett-Teller (BET) method. The total pore volume (V_{total}) was obtained as the volume of liquid nitrogen adsorbed at a relative pressure of 0.98. The pore size distributions of sorbents were derived from the desorption branches of isotherms based on Barrett-Joyner-Halenda (BJH) theory. Thermogravimetric Analysis (TGA) was carried out with a NETZSCH STA 449 C thermal graphic analyzer using a heating rate of 10 K/min in N_2. Attenuated Total Reflection Infrared (ATR-IR) spectrum of TETA was determined on a Nicolet 670 FTIR spectrometer equipped with an ATR-IR accessory. Fresh PTNT and TETA-impregnated sorbents were additionally characterized by transmission infrared spectroscopy carried out on the pellets. The ^{13}C CP/MAS NMR experiment was conducted on a Bruker AVANCE 400. The spinning frequency was set to 8 kHz. The contact time was 14.85 ms, with recycle delays of 3 s.

2.5. CO_2 adsorption and sorbents regeneration

The CO_2 adsorption capacities of the sorbents were carried out in a fixed-bed reactor system as shown in Fig. S1 (supplementary materials). The adsorption process was done at atmospheric pressure and the outlet gases were monitored online by using an Agilent 7820A gas chromatograph with a thermal conductivity detector (TCD). The online GC can automatically do continuous measurement even with up to 300 data points per minute. Based on the signal changing on the TCD detector, CO_2 breakthrough curve was achieved. About 0.5 g dried adsorbent was packed into the middle of the quartz-tube reactor (6 mm inner diameter) and heated by heating tapes. Before each adsorption test, the adsorbent was activated by heating it to 100 °C and maintained in N_2 stream for 1 h with a flow rate of 20 mL/min. After the sorbent cooling to the desired adsorption temperature (e.g., 75 °C), a mixture of 10% CO_2 balanced with N_2 stream at a total flow rate of 10 mL/min was introduced and passed through the adsorbent bed until it reached adsorption saturation. The CO_2 breakthrough capacity of adsorbents was calculated by integrating the breakthrough curve along with the subtraction of blank.

In the multiple cyclic adsorption-desorption test, each sample was first activated at 100 °C for 1 h in N_2. Then, it was cooled down to 75 °C, at which temperature CO_2 adsorption was performed under 10% CO_2/N_2 flow (10 mL/min). Following that, the sorbent regeneration was carried out under N_2 (20 mL/min) through the bed at 100 °C for 1 h. The same adsorption-desorption procedure was conducted for 6 cycles in order to test the stability of the sorbent.

3. Results and discussion

3.1. Characterization of sorbents

The morphology of PTNT (T2 as the representative case) was examined by SEM and TEM, respectively. We can see many irregular aggregations of PTNTs in Fig. 1a. On close observation, Fig. 1b and c reveal that the surfaces of these aggregations contain a large number of scattered and overlapped one-dimensional structures.