

Polyethylenimine-incorporated zeolite 13X with mesoporosity for post-combustion CO₂ capture



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ARTICLE INFO

Article history:

Received 15 December 2014

Received in revised form 14 January 2015

Accepted 16 January 2015

Available online 23 January 2015

Keywords:

13X

Mesoporosity

Polyethylenimine

CO₂ capture

Post-combustion

ABSTRACT

X-type zeolite with mesoporosity (Meso-13X) was prepared by using dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride as a mesopore-generating agent, and then modified with polyethylenimine (PEI) through a physical impregnation method to form a hybrid material (Meso-13X-PEI). Meso-13X with and without PEI was characterized by X-ray powder diffraction (XRD), N₂ adsorption-desorption isotherm at 77 K, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Meso-13X-PEI exhibited higher CO₂ capture capacity than PEI-modified zeolite 13X owing to its larger pore volume that accommodates more amine species inside the pore structure, and the mesoporosity also can facilitate dispersion of PEI molecules inside the pore channels. Compared to zeolite 13X, Meso-13X-PEI showed much higher CO₂ capture selectivity (against N₂) as well as higher CO₂ capture capacity at relatively high temperature (e.g. 100 °C) and dilute CO₂ concentration relevant to post-combustion conditions.

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1. Introduction

Anthropogenic CO₂ emissions to the atmosphere, largely produced by combustion of fossil fuels, are causing increased public concern due to consequence of global climate change [1]. Carbon capture and sequestration has been considered to be one approach that holds great promise for reducing CO₂ emissions [2]. Among several alternatives that can be pursued for capturing CO₂ from the coal-derived power generation, post-combustion carbon capture has the greatest near-term potential, since it can be retrofitted to existing units that generate about two-thirds of the CO₂ emissions in the power sector [3]. CO₂ capture based on adsorption principle is considered to be more convenient and energy-efficient than conventional absorption processes that use corrosive basic liquid amine species [4,5]. As depicted in Fig. 1, the post-combustion capture concept involves the removal of CO₂ from the flue gas produced by combustion. The typical temperature of thermal power plant flue gas is around 140 °C, and the flue gas typically has a CO₂ concentration of less than 15%, with mostly N₂ in balance with ca. 10% moisture. Therefore, it would be desirable to devise a CO₂-selective adsorbent that can operate close to such set of conditions. An

adsorbent operating at the lower temperature would need an energy demanding cooling step prior to the CO₂ capture.

Zeolites have been widely investigated as a CO₂ adsorbent [6–11], especially zeolite 13X, which has been considered to be a benchmark material for CO₂ capture owing to its high CO₂ capture capacity [6–8]. However, zeolites are usually utilized as CO₂ adsorbents at low or ambient temperatures due to the thermodynamics of the physical adsorption involved, and low CO₂ capture selectivity toward N₂ is another disadvantage for their application in post-combustion systems. To remedy these problems, several groups have been investigating incorporation of amine species into the pore structure of zeolites to make a hybrid adsorbent for CO₂ capture [12–16]. Jadhav et al. impregnated monoethanol amine (MEA) onto zeolite 13X and examined the resultant hybrid material for CO₂ adsorption at different temperatures [12]. The MEA-impregnated adsorbent showed higher CO₂ capture capacity than bare zeolite 13X at 120 °C, and also exhibited improved CO₂ capture selectivity. Su et al. similarly modified a commercial Y-type zeolite by tetraethylenepentamine using a physical impregnation method [13]. The CO₂ adsorption capacity of the hybrid adsorbent increased with increasing temperature at 30–60 °C but decreased between 60 and 70 °C. Xu et al. examined the adsorptive separation of CO₂, CH₄ and N₂ on MEA-modified β-zeolite [14], and found that the incorporation of MEA improved both CO₂/CH₄ and CO₂/N₂ selectivity. Apparently, hybrid materials prepared through

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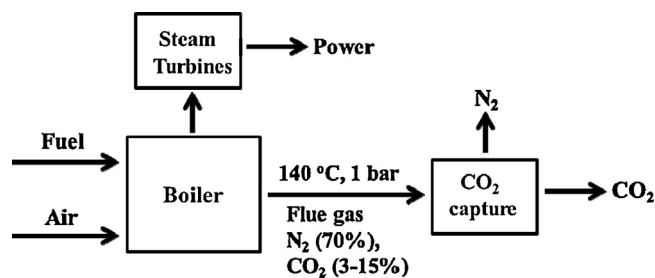


Fig. 1. A simplified block diagram illustrating a typical post-combustion CO₂ capture system in power plants.

impregnation of amine species into a zeolite show good CO₂ capture capacity at relatively high temperatures and improved CO₂ capture selectivity toward other gases, meeting those requirements for post-combustion CO₂ capture system. These amine species incidentally are also known to increase the CO₂ capture capacity in the presence of moisture [17].

A weakness of the zeolites as a porous support material, however, is their small pore volume and pore size, which is unfavorable for amine incorporation inside the pore structure, i.e., small pore volume sets a limit to the amount of amine species that can be incorporated, and small pore size hindering better dispersion of amine species inside the microporous pore channels. In this work, we synthesized a hierarchical zeolite X with mesoporosity (Meso-13X) and attempted to make use of the mesoporosity to incorporate increased and better dispersed amine species inside its pore structure. Polyethylenimine (PEI) was chosen as the amine source, which was found to greatly enhance CO₂ capture when supported on mesoporous silica [18–23]. The effectiveness of PEI-modified Meso-13X (Meso-13X-PEI) as a CO₂ adsorbent was tested in terms of its adsorption capacity, selectivity and stability. For this purpose, we measured CO₂ adsorption capacities gravimetrically under different conditions of temperatures and CO₂ partial pressures. The CO₂ capture performance of zeolite 13X and PEI-modified commercial zeolite 13X (13X-PEI) were also tested for comparison.

2. Experimental

2.1. Materials

Sodium silicate solution (SiO₂ ~26.5 wt%, Na₂O ~10.6%, Sigma–Aldrich), sodium aluminate (Na₂O 42.5 wt%, Al₂O₃ 53.0 wt%, Riedel-de Haën), sodium hydroxide (97%, Dae Jung), dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC, 60% in methanol, ACROS), Polyethylenimine (PEI, ethylenediamine branched, average Mw ~800 by LS, average Mn ~600 by GPC). Zeolite 13X was also purchased from Sigma–Aldrich.

2.2. Synthesis

2.2.1. Meso-13X

Meso-13X was synthesized following the method of Inayat et al. [24]. Sodium silicate solution, NaOH and distilled water were mixed at room temperature before sodium aluminate solution was added under vigorous stirring. After the mixture was stirred for 1 h, TPOAC was added. The obtained gel with molar composition Al₂O₃:3.5Na₂O:3SiO₂:180H₂O:0.06TPOAC was aged for 1 day at room temperature and statically crystallized at 75 °C for 4 days in a convection oven. The product was filtered, washed with distilled water and dried. The organic template was removed by calcination at 650 °C for 8 h in 80 ml/min air flow.

2.2.2. Polyethylenimine-modified zeolites

PEI was introduced to commercial 13X and Meso-13X samples through a physical impregnation method proposed by Xu et al. [18]. In a typical preparation, PEI was dissolved in methanol with constant stirring for approximately 30 min, after which zeolite samples were added to the PEI/methanol solution. The resulting slurry was stirred continuously for approximately 1 h, and heated to 70 °C for 16 h under reduced pressure (700 mmHg). In this study, the amine amount introduced to zeolite samples was adjusted to match the pore volume of the zeolite samples, since the optimal amine loading level was confirmed by several research groups to be the one corresponding to the amount required to fill up the pore volume of the host materials [12,15,18]. The PEI-impregnated zeolite samples were designated as 13X-PEI and Meso-13X-PEI, respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku diffractometer using CuKα ($\lambda = 1.54 \text{ \AA}$) radiation. Nitrogen adsorption–desorption measurements were carried out on a Belsorp(II)-max at 77 K. Surface area was calculated by the BET (Brunauer, Emmett, and Teller) method. For Meso-13X, the total pore volume was estimated from the N₂ adsorbed amount at $P/P_0 = 0.995$, mesopore volume from the BJH cumulative curve, and the micropore volume was estimated by the difference. For commercial 13X, pore volume was calculated using MP method from a t -plot. The mesopore size distribution was estimated based on the BJH (Barrett–Joyner–Halenda) model. The morphological features were examined by scanning electron microscopy (SEM, Hitachi S-4300). The amine loading amount on zeolites was measured by thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000) by heating the samples to 600 °C with air flow.

2.4. CO₂ adsorption–desorption measurement

The TGA unit (SCINCO thermal gravimeter S-1000) connected to a flow panel was used to conduct CO₂ adsorption–desorption experiments. Samples were all pretreated at 100 °C before commencing CO₂ adsorption measurements. The adsorption run was carried out using high purity CO₂ (99.999%, U-Sung) or 15% CO₂ (85% N₂ as balance) gas, and Ar (Ultra high purity, 99.999%, U-Sung) was used as purge gas. A feed flow rate of 30 ml/min to the sample chamber was controlled with a MFC (Mass Flow Controller).

3. Results and discussion

3.1. Characterization of materials

Fig. 2 shows the XRD patterns of the zeolite samples prepared. Meso-13X and Meso-13X-PEI exhibited practically identical XRD patterns to that of 13X, only with slightly decreased peak intensities, indicating that the framework structure was preserved after introducing mesoporosity or after subsequent amine incorporation. Fig. 3a shows the N₂ adsorption–desorption isotherms of the corresponding samples. 13X showed typical type I isotherm, reflecting its microporous structure. For Meso-13X, microporosity was evident from the type I isotherm at low relative pressure range ($P/P_0 < 0.1$); at higher pressure range ($0.4 < P/P_0 < 1$), a hysteresis loop with capillary condensation indicated the mesoporosity, which was further demonstrated by the BJH pore size distribution of Meso-X (Fig. 3b) centered around 6 nm. The N₂ adsorbed amount by the Meso-13X-PEI was almost none, indicating that pore volume was filled-up after PEI incorporation. Corresponding textural properties of the samples were summarized in Table 1, which showed that ca. 46% of the total pore volume is comprised mesoporosity

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