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Synthesis of SAPO-34 with alkanolamines as novel templates and their application for CO_2 separation

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ABSTRACT

Alkanolamines are used for the first time as both the solvent and template to explore the syntheses of SAPO molecular sieves. Diglycolamine (DGA) and diisopropanolamine (DIPA) are found to act as novel structure-directing agent for the synthesis of SAPO-34, and N-methyldiethanolamine leads to the crystallization of SAPO-44. The obtained SAPO-34s are well characterized and investigated as adsorbents for selective separation of CO_2 from N_2 and CH_4. A close relationship between the acid concentration of SAPO-34 and CO_2 adsorption capacity has been revealed. SAPO-34-DGA with the highest acid concentration (sample D4) exhibits the best CO_2 adsorption capacity and high CO_2-over-N_2 selectivity. Breakthrough experiments are further carried out based on sample D4, which shows an excellent dynamic preferential adsorption ability for CO_2 (~8.2 wt%) from both CO_2/N_2 and CO_2/CH_4 mixtures (298 K). These results demonstrate that SAPO-34-DGA could be a promising adsorbent for the CO_2 capture.

1. Introduction

Molecular sieves are an important class of crystalline microporous inorganic materials, which have been widely applied in industry as catalysts, ion exchangers, and adsorbents [1–3]. For the past three decades, the development of molecular sieve synthesis has greatly extended their framework types and compositions, and more than 200 zeotype structures have been identified [4]. Any progress in the field of molecular sieves might promote motivate their innovative application and establish some new industrial processes. Therefore, it is always attractive to explore new zeotype materials and novel synthetic methodologies [5].

SAPO-34 molecular sieve, first reported by the scientists of Union Carbide Company in the 1980s [6,7], is one of the most important members in the silicoaluminophosphate molecular sieve family. It has exhibited excellent performance in the methanol-to-olefin (MTO) reaction [8,9] and good selective separation capacity for CO_2 from CH_4 or N_2 [10–12]. The synthesis of SAPO-34 could be fulfilled by many strategies, including hydrothermal method [6–12], solvothermal method [13,14], and dry-gel conversion [15]. Very recently, an interesting solvent-free synthesis method has also been developed by Xiao et al. [16]. Meanwhile, multiple templates have showed structure-directing ability to the synthesis of SAPO-34 such as tetraethylammonium hydroxide (TEAOH) [17], morpholine (MOR) [18], piperidine [19], dipropylamine [20], triethylamine (TEA) [21] and diethylamine (DEA) [22]. It is well acknowledged that SAPO-34 crystallized with different templates might leads to different morphology, microstructure, and Si coordination environment (acidic property), and thus differs in their catalytic properties. For example, TEAOH is capable to direct the synthesis of SAPO-34 nanocrystals with long lifetime and high selectivity to light olefins in the MTO reaction [17]. While both MOR and DEA tend to synthesize micro-sized SAPO-34 crystals with high Si incorporation into the framework [18,22]. These kinds of SAPO-34s generally exhibit shorter lifetime in the MTO reaction than SAPO-34 templated by TEAOH [17,22,23]. Barthomeuf et al. have made pioneering research about the relationship between template types and Si environments. They found that the templates in the cages of SAPO-34 were essential for the compensation of framework charges produced by the silicon incorporation accompanied by the generation of Brønsted acid sites via SM2 mechanism or SM2–SM3 combination. The template number per cage was mainly determined by the molecule size of organic amine, which had a great effect on the maximum concentration

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of single Si environment in the framework. That is, the more amine molecules occluded in the cage, the higher single Si (4Al) concentration in the framework [24,25].

Nowadays, selective separation of CO_2 from gas streams is of paramount importance since its accumulation in environment can cause severe global warming [26,27]. Besides, the removal of CO_2 from CH_4 is an attractive issue in the processing of natural gas, because that the existence of CO_2 in natural gas will reduce the energy content and its acidity caused by water will lead to pipeline corrosion [28,29]. Currently, the technology based on absorption in aqueous solution of alkanolamines has been commercialized, but this method is very complex and produces corrosion for the equipment [30]. It is highly desirable to develop adsorption processes with porous materials as adsorbents, such as pressure swing adsorption (PSA), in which less energy consumed and no chemical solvents required. Compared with other nanoporous adsorbents, molecular sieves offer many advantages such as adjustable pore apertures, moderate surface polarity, and good thermal/hydrothermal stability. Many research works have been reported on the adsorption behaviors of zeolites A, X, Y, RHO, ZK-5, and chabazite etc. [31–36]. The adsorption properties of zeolites can be modified by changing the cations inside the channels or cages of zeolites [37,38]. In addition, SAPO molecular sieves also attract interests as CO_2 adsorbents. The electrostatic interaction of SAPO frameworks with CO_2 is generally weaker than that of zeolites, which may benefit the regeneration of adsorbents. Hedin once compared the water adsorption isotherms of SAPOs with that of zeolite 13X and claimed that SAPO molecular sieves are less moisture-sensitive than 13X, which is important to the practical application of SAPO adsorbents [39].

Among SAPO molecular sieves, SAPO-34 is one of the most intensively studied whatever in swing adsorption process or membrane separation [40,41]. The good properties of SAPO-34 in adsorption/separation are believed to be arising from its large pore volume and suitable pore diameter (0.38 nm), which is close to the kinetic diameter of CH_4 (0.38 nm) but larger than that of CO_2 (0.33 nm). Many methods such as extra-framework cation modification and amine functionalization have been explored to improve the CO_2 adsorption capacity or separation selectivity on SAPO-34 [42,43]. However, the influence of the acid properties of SAPO molecular sieves on the gas adsorption has draw less attention though acid sites of SAPO molecular sieves were evidenced to be the preferential adsorption sites for CO_2 [39,44]. An interaction between the acidic hydroxyl group and CO_2 ($H^+\cdots O(CO_2)$) has been proposed and rationalized by theoretical calculations [45].

Recently, a novel aminothermal synthesis method has been developed by our laboratory, where organic amines playing as both the solvent and template lead to the crystallization of SAPO molecular sieves with high yields and good properties [13,14]. Herein, alkanolamines, combining the properties of amine and alcohol [46], are used for the aminothermal synthesis of SAPO molecular sieves. Fortunately, several alkanolamines are found as novel templates to direct the structure of SAPO-34 and SAPO-44 molecular sieves. The obtained SAPO-34s with different Si contents are explored for CO_2 separation, and one of them shows excellent performance.

2. Experimental

2.1. Sample preparation

All alkanolamines used in the synthesis were analytically reagents. Silica sol (30.3 wt%), pseudoboehmite (72.5 wt%) and phosphoric acid (85 wt%) were used as inorganic reactants.

Eight kinds of alkanolamines, including triethanolamine (TEOA), diethanolamine (DEA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine(DEAE), N-methyldiethanolamine (MDEA), and diglycolamine (DGA), were tried to aminothermally synthesize of SAPO molecular sieves.

A typical synthesis procedure was as follows: alkanolamine, water, pseudoboehmite and silica sol were added in sequence into a glass beaker. The mixture was stirred at room temperature for 10 min, and then transferred into a stainless steel autoclave. Subsequently the phosphoric acid was added into the mixture drop by drop with stirring and a homogeneous and viscous mixture was obtained, following which the autoclave was sealed quickly and placed in an oven. After the autoclave being rotated at 50 rpm for 30 min to get a more homogeneous mixture, it was heated to 473 K within 90 min under rotation and kept for 48 h. At the end of the crystallization, the products were recovered by filtration with distilled water, and dried at 393 K in air. As-synthesized materials were calcined in air at 823 K for 2 h to obtain the template-free samples.

2.2. Characterizations

The powder XRD patterns were recorded on a PANalytical X′ Pert PRO X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.54059$ Å), operating at 40 kV and 40 mA. The chemical composition of the samples was determined with Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by field emission scanning electron microscopy (Hitachi, SU8020). All the solid state NMR experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequencies were 600.13, 156.4, 242.9 and 119.2 MHz for ^{1}H, ^{27}Al, ^{31}P and ^{29}Si, respectively. ^{27}Al and ^{31}P MAS NMR experiments were performed on a 4 mm MAS probe with a spinning rate of 12 kHz. ^{27}Al MAS NMR spectra were recorded using one pulse sequence. A 200 scans were accumulated with a $\pi/8$ pulse width of 0.75 μs and a 2 s recycle delay. Chemical shifts were referenced to $(NH_4)Al(SO_4)_2{\cdot}2H_2O$ at −0.4 ppm. ^{31}P MAS NMR spectra were recorded using high-power proton decoupling. A 100 scans were accumulated with a $\pi/4$ pulse width of 2.25 μs and a 4 s recycle delay. Chemical shifts were referenced to 85% H_3PO_4 at 0 ppm. ^{29}Si MAS NMR spectra were recorded with a 7 mm MAS probe with a spinning rate of 6 kHz using high-power proton decoupling. A 5000–6000 scans were accumulated with a $\pi/4$ pulse width of 2.5 μs and a 10 s recycle delay. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS). ^{1}H MAS NMR spectra were recorded using a 4 mm MAS probe. The pulse width was 2.2 μs for a $\pi/4$ pulse, and 32 scans were accumulated with a 4 s recycle delay. Samples were spun at 12 kHz, and chemical shifts were referenced to adamantane at 1.74 ppm. Before ^{1}H MAS NMR measurements, the samples were dehydrated typically at 693 K under pressure below 10^{-3} Pa for 20 h. The software Dmfit was employed for deconvolution using fitting of Gaussian–Lorentzian lineshapes. For the determination of quantitative results, all samples were weighed, and the spectra were calibrated by measuring a known amount of adamantine performed in the same conditions. N_2 adsorption–desorption isotherms were obtained on a Micrometrics ASAP 2020 system at 77 K. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evacuated using the *t*-plot method. The thermal analysis was performed on a TA Q-600 analyzer with a temperature-programmed rate of 10 K/min under an air flow of 100 ml/min. The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out with an Autochem 2920