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Short communication

Ultrafast microwave synthesis of all-silica DDR zeolite

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ABSTRACT

Non-seeded ultrafast microwave synthesis of all-silica DDR zeolite was realized using 1-adamantane amine and tetraethylammonium hydroxide. XRD, SEM, NMR, FT-IR, TGA and nitrogen adsorption were used to characterize the obtained samples. The presence of TEAOH suppressed the formation of other phases which allowed the synthesis to be carried out at high temperature. High quality DDR crystals were obtained in only 30 min without seeding, which is the fastest synthesis up to now. 1-Adam serves as template for zeolite DDR and TEAOH is not occluded in zeolite channels. The ultra fast synthesis is the synergy of fast heating from microwave energy, fast kinetics (nucleation and crystallization) at high temperature and phase selectivity from the TEAOH. The obtained DDR crystals have similar properties as those prepared with traditional method.

1. Introduction

Zeolites/molecular sieves have numerous applications in various industries for separation and catalysis due to their uniform molecular sized pores, tunable acidity and unique adsorption property [1]. Taking advantage of zeolites's unique pore system, adsorption property and great stability, zeolite membranes have great potential to separate various gas or liquid mixtures through the difference in adsorption and diffusion [2–5]. Among various types of zeolite membranes investigated, small pore zeolite membranes (zeolite with 8-MR) are especially interesting, such as SAPO-34 [6–14], high silica CHA [15–17] and DDR membranes [18–22], because their pore sizes are perfect for many important industrial separation processes, like CO_2–CH_4 separation. All-silica DDR (Si-DDR) membranes, with pore aperture ~0.36 × 0.44 nm, allows the selective diffusion of CO_2 (kinetic diameter 0.33 nm) to the inner pore structure, while excludes the larger CH_4 (0.38 nm) molecule [6]. The all-silica hydrophobic framework gives DDR membrane great stability and insensitivity to the moisture in the feed stream, which is superior to other hydrophilic zeolite membranes.

Despite the huge potential applications of DDR zeolite and membrane, the synthesis of zeolite DDR was a daunting task in the following aspects, such as long synthesis time, poor reproducibility, lack of control of crystal size and morphology [23–31]. Gies et al. first reported the synthesis of DDR in 6–9 weeks [23]. Den Exter et al. optimized the synthesis and obtained pure DDR crystals in 25 days [24]. Tomita et al. prepared DDR membranes in 2 d by secondary growth method, which indicated that seeding can significantly reduce the synthesis time [19]. Gascon et al. reduced the synthesis time of DDR powder from 25 d to 2 d by adding 0.02 wt% seeds to facilitate nucleation [25]. Yang et al. obtained DDR in 9 d (no seeding) or 1 d (with the aid of seeding) with the addition of KF as mineralizing agent [26]. Gucuyener et al. found the proper cleaning of Teflon liner eliminates the memory effect (or the interference of other phase) and thus improves the reproducibility [27]. Sen et al. prepared DDR zeolite at room temperature in 2–5 d by sonochemical method (without seeding) [30].

In our continuous effort to simplify the synthesis of all-silica DDR, we significantly shortened the synthesis time from 25 d to 2 d with microwave aided hydrothermal synthesis (no seeding) [32]. Then, with $(NH_4)_2SiF_6$ as silica source, the synthesis time was further reduced to 12 h with regular hydrothermal synthesis (no

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seeding) [33]. In this communication, we propose the ultrafast seedless microwave-aided hydrothermal synthesis of all-silica DDR zeolite using a mixture of 1-Adam and TEAOH. The obtained DDR samples were characterized by XRD, SEM, NMR, nitrogen adsorption, FT-IR and thermal analysis.

2. Experimental methods

2.1. Chemicals

1-adamantane amine (1-ADA, 99 wt%) was provided by Shanghai Nuotai Chemical Corporation. Tetraethylammonium hydroxide (TEAOH, 35 wt% aqueous solution) was provided by Shanghai Richjoint Chemical Reagents. Tetrametylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide were obtained from Shanghai Richjoint Chemical Reagents (all in the form of 20 wt% aqueous solution). Silica sol (Ludox AS-40, 40 wt% SiO_2) was obtained from Sigma–Aldrich. All chemicals were used without further purification.

2.2. Ultrafast synthesis of zeolite DDR

Zeolite DD3R was synthesized from precursor with molar recipe of $1SiO_2$: 50–$100H_2O$: 0.5ADA: 0.2TEAOH. In a typical synthesis, ADA and silica sol were mixed and stirred for 1 h, followed by addition of TEAOH and 30 min stirring. The precursor was loaded into an autoclave and heated at 200–220 °C for different durations with microwave heating ((Milestone Ethos A advanced microwave system, with stirring). The solids obtained were thoroughly washed, dried and then calcined at 900 °C in air for 24 h to remove the template.

2.3. Characterization

Powder XRD patterns were collected by a Rigaku Ultima IV X-ray diffractometer with Cu Kα X-radiation (tube voltage: 40 kV and tube current: 40 mA). Scanning electron micrographs (SEM) were taken on a ZEISS SUPRA55 SAPPHIRE field emission scanning electron microscope at 2 kV. Samples for SEM analysis were coated using a Shanghai Fudi sputter coater with a gold-palladium target. ^{29}Si MAS NMR measurements were performed on a Bruker Advance-400 spectrometer operating at 99 MHz. The NMR spectra with high-power proton decoupling were recorded by the use of a sample-rotation rate of 5 kHz and a 4 mm MAS probe head. Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier-transform infrared spectrometer (FT-IR). Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer Pyris 1 thermogravimetric analyzer at a heating rate of 10 °C/min under flowing air. Nitrogen adsorption measurements were carried out on a Micromeritics TriStarII3020 surface area analyzer. The analyses of the calcined samples were acquired after outgassing at 300 °C.

3. Results and discussion

3.1. Effect of H_2O/SiO_2 ratio

Fig. 1 and Fig. 2 show the effect of synthesis time on the powder XRD patterns and SEM images of samples prepared with gel molar recipe of $1SiO_2$: $100H_2O$: 0.5ADA: 0.2TEAOH (MW at 493 K, no seeding). As shown in Fig. 1, the sample was amorphous after 15 min at 493 K, but characteristic DDR peaks were observed after only 20 min. Extension of synthesis time to 30 min and 60 min, high quality XRD patterns without impurity were obtained. The yield of DDR increased fast from 8% (20 min) to 10% (30 min) and 76% (60 min), respectively. The SEM images in Fig. 2 show similar trend.

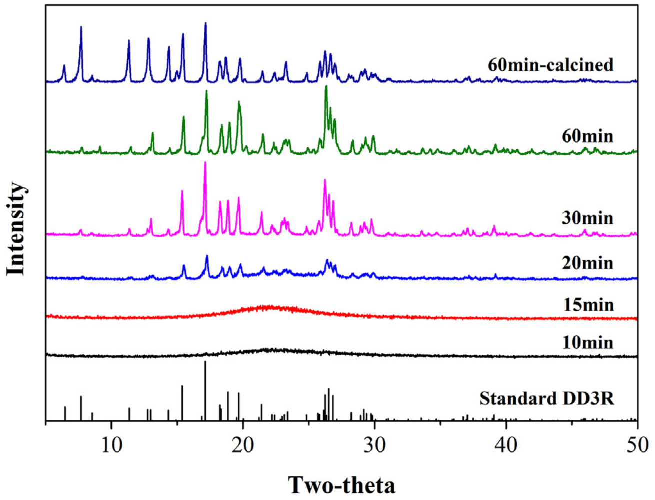

Fig. 1. The effect of synthesis time on the XRD patterns of DDR samples ($1SiO_2$:$100H_2O$:0.5ADA:0.2TEAOH, MW at 493 K).

After 20 min, characteristic rhombohedral & polyhedral crystals were easily observed along with lots of un-converted amorphous silica. The content of amorphous silica decreased fast with synthesis time and the crystal size increased substantially from 4 μm (20 min) to 6 μm (40 min) and 10 μm (60 min). At 60 min, well-developed rhombohdral DDR crystals were obtained with high yield (76%). Further increase of synthesis led to little change of crystalinity and yield.

NMR is a powerful technique to reveal differences in the local chemical environment of framework atoms in zeolites, so ^{29}Si MAS NMR spectra of calcined DDR samples were acquired (shown in Fig. 3). Similar to literature result [32,33], five major peaks at −112.8, −113.5, −119.2, −121.3 and −122.7 pm were observed in the typical Q^4 range. These signals represent various $[SiO_4]$ sites with different atomic and displacement parameters. The peak at −121.3 ppm can be assigned to silicon sites in the 8-membered rings connecting the cages and the windows. No peaks were observed in the typical Q^3 range (−90–−100 ppm, corresponding with $Si-(OSi)_3OH$), which indicates a defect-free silicate structure [33]. This result indicates that DDR framework started to form after 20 min synthesis, consistent with the XRD and SEM results shown in Figs. 1 and 2.

Fig. 4 depicts the IR spectra of DDR samples(as-prepared and calcined). The high-frequency bands at 1115 and 803 cm^{-1} corresponded to silicon and oxygen motion, respectively. The peaks at 523 cm^{-1} came from the inter-tetrahedral double ring linkages of the zeolite structure. The bands at ca. 455 and 788 cm^{-1} (as-prepared and calcined samples) can be attributed to Si–O–Si bending and Si–O tetrahedral vibration, respectively. Apparently, the peaks associated with framework atom vibrations were observed after 20 min synthesis, which is another evidence of the formation of DDR framework. The bands at 2851 and 2931 cm^{-1} can be ascribed to the CH and CH_2 stretching vibrations from the 1-Ada (organic template in the as-prepared sample). After calcination, the peaks associated with 1-Ada disappeared (~2900 cm^{-1}), which indicated the complete template removal. The absence of characteristic peaks from TEAOH suggests that only 1-Ada serves as organic template and TEAOH was not occluded in zeolite crystals. The hydrophobicity of the calcined DDR was confirmed by the weak adsorption at ~3000 cm^{-1} (from −OH vibrations) which showed little adsorption of water [33].