Controlable synthesis of Si-DD3R molecular sieves nanocrystalline by microwave assisting dry-gel conversion method

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Abstract
All-silica Deca-Dodecasil 3 Rhombohedral (Si-DD3R) type zeolite with a two-dimensional pore system is a very attractive size selective adsorbent which enables only small molecules to adsorb. It is a great potential candidate in the fields of separation and catalysis. In this work, nanocrystalline Si-DD3R molecular sieves with the particle size of about 30 nm were synthesized by microwave assisting dry-gel conversion (MADGC) method. The advantages of microwave radiation, HF and dry-gel conversion (DGC) were well combined and effectively decrease the size and in situ synthesis time. At 433 K, highly uniform nanocrystalline Si-DD3R was obtained in 7 h without seeding. When the partial pressure was 1.0 bar, the CO2 adsorbed amount reached about 0.83 mmol g⁻¹. The zeolites are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

1. Introduction

Nanocrystalline zeolites (with crystal sizes of 100 nm or less), which have many advantages over conventional micron sized zeolites of larger external surface areas, shorter diffusion path-lengths and lower tendencies to form coke [1, 2]. They have received much attention due to their great potential application in catalysis and adsorption [3]. In addition, they can be used for preparation of zeolite films and membranes as well as composites, hierarchical structures and so on [4]. Pure silica nano-sized zeolites have becoming promising as low-dielectric constant materials in electronics applications [5]. Generally, nanozeolites have been prepared by various alternative methods [6] such as conventional hydrogel synthesis [7], confined synthesis [8] microreactor [9], seed assisted approach [10], microwave [10, 11, 12]/sonication [13]. These water mediated hydrothermal methods were well addressed in the reviews by V P Valtchev and L Tosheva [14]. In addition, DGC [15] are reported for the synthesis of nano-sized zeolites. Up to now, many kinds of nanozeolites have been formed, like types FER [16], SAPO-34 [17], MFI [18], BEA [15], et al. [19].

In contrast to hydrothermal synthesis, DGC converts a dry gel to zeolites in the presence of steam, sometimes, with structure directing agents (SDA) in the vapor phase. It is effective alternative route for synthesis of zeolites especially for some particular phases and properties [19], because it can provide a better control on the reactants selection and adjust the desired ratios. Importantly the nucleation and crystallization of zeolites synthesis are separated by the DGC method, which is beneficial for preparing nanocrystals [15, 20]. Whereas, there was only a few reports about the synthesis of nano-sized Si-DD3R zeolites which indicated that such nanocrystallines were probably difficult to synthesize.

DD3R type zeolites have a two-dimensional pore system connect to an 8-ring with an aperture of 4.4 × 3.6 Å, which enables only small molecules to adsorb and with a very attractive size selective adsorbent. A great potential in the fields of separation and catalysis of DD3R topology was exhibited in the high selective adsorption of propylene over propane [21], trans-but-2-ene and buta-1,3-diene over other butane and but-2-ene isomers [22], CO2/CH4 [23-25], CO2/N2 [26], and self-diffusion of small hydrocarbons [27, 28]. Although
Si-DD3R zeolites presented these excellent properties, the extremely long crystallization time and complex reactions involved make the synthesis of pure Si-DD3R very challenging. D1H (DOH) and Sigma-2 (SGT) as the primary competitive phases might also occurred during the Si-DD3R formation due to the similar synthesis composition of them [22]. Different strategies from adjusting of growth pH [21], improving solubility of 1-Adamantane amine (ADA) template in water [29] with addition of EDA or KF to use of seeds have been proposed to inhibit the growth of DOH and SGT for achievement of a pure Si-DD3R phase and short of the synthesis time. Although the efforts on the Si-DD3R study, the investigation on nano-sized Si-DD3R zeolites was lack probably due to its complex framework topology and formidable control. Only MitaliSen [30] reported the preparation of nano-DD3R zeolite of 100 nm in sonochemical reaction.

Herein, a new strategy of microwave assisting dry-gel conversion (MADGC) was proposed to prepare nano-sized Si-DD3R. The as-synthesized zeolites were uniform and the particle size was about 30 nm. As illustrated in figure 1, the synthesis precursor gel containing silica source, ADA template, EDA and HF was treated in the radiation of microwave for a specific period. The motivation of the use of the microwave is to facilitate formation of plenty of nuclei of Si-DD3R, decrease the process time and consume less energy, because the microwave could increase the heating rate and provide homogeneous heat [12]. Then the microwave treated gel was dried and triturated into powder. The dried gel powder was subject to crystallization conversion with the assistance of water steam. DGC is expected to facilitate the crystal growth of Si-DD3R and reduce the synthesis time. In this way, this MADGC strategy is expected to lead to synthesis of nano Si-DD3R zeolites because the plenty of nuclei are favourable for the growth of nano zeolites. The effects of fluorine source on the formation of nano Si-DD3R were also examined.

2. Experimental

2.1. Materials
Chemicals were used as received: 1-Adamantane amine (1-ADA, Sigma Aldrich, 97%), ethylenediamine (EDA, Sigma Aldrich, 99%), silica source (Ludox AS-40 colloidal silica, P40%), potassium fluoride (KF · 2H2O, Tianjin Kemiou Chemical Reagent Co., Ltd), Hydrofluoric acid (HF, Sigma Aldrich, 48%), hydrochloride (HCl, Shantou Xilong Chemical Reagent Co., Ltd, P38%), deionized water (home-made).

2.2. Controllable synthesis of Si-DD3R zeolites
The synthesis mixture molar ratio of 47 ADA:100 SiO2:404 EDA:11240 H2O: 50 HF was prepared as follows. ADA was dissolved in EDA and water was then added rapidly. This mixture was subject to the radiation of ultrasonic machine for 1 h, specific amount of colloidal silica was added into the mixture under vigorous stirring followed by refluxing at 368 K for 2 h and then cooling down to room temperature. Subsequently HF was dropwise added into the mixture and kept under stirring for 3 h. The microwave treatment (with a MWD-520 microwave system at the frequency of 2450 MHz, Shanghai Metash Instrument Co., Ltd, China) for the obtained precursor gel was performed at 433 K for 7 h. Drying this microwave treated gel and triturated it into powders then put them into the stainless-steel autoclave and the powders and water were separated by a Teflon holder. The dried powders were subject to the DGC with assistance of steam for crystalline transform of Si-DD3R at 433 K for 4 days conversion. In this way, during which the steam from the water at the bottom of the autoclave
contacted with the upper dried precursor gel to facilitate the crystallization process of the zeolites and the products were obtained. After drying, the powder product was calcined in air at 973 K for 7 h to remove the organic components.

2.3. Characterizations

The structure of the crystals were identified by XRD using a Rigaku-Dmax 2400 diffractometer with graphite monochromated Cu Kα radiation in a range of 5°–50°. The size and the morphology of particles were observed on a NOVA NANOSEM 450 (FEI Company) with the accelerating voltage of 10 kV after gold coating. TEM of the nanocrystal was carried out on a Tecnai F30 instrument, operating at 300 kV. The CO₂ adsorption performance was tested by specific surface area aperture analyzer (V-Sorb-2800P, APP application, Beijing). The sample weight of adsorbent was fixed 0.1 g while the temperature was 298 K.

3. Results and discussion

3.1. Characterization of DD3R-type zeolite with microwave assisting

Figure 2(a) shows XRD pattern of the sample synthesized by MADGC at 433 K for 4 days conversion, with a molar ratio of 47 ADA:100 SiO₂:404 EDA:1124 H₂O:120 HF in starting gel. It was obviously to see that all of the peaks can match the DD3R standard pattern with a characteristic peak of the amorphous phase slightly observed. So the pure Si-DD3R molecular sieves with a relatively high crystallinity was obtained. A clear broadening of the reflections was observed which attributed to small crystals. Furthermore, the SEM image of the sample (figure 2(b)) shows that the particles distribute very well with the uniform size about 30 nm. All these results indicate that a pure phase Si-DD3R could be obtained during MADGC. In this way, the dried powders were subject to the DGC with assistance of steam for crystalline transform of Si-DD3R, during which the steam from the water at the bottom of the autoclave contacted with the upper dried precursor gel to facilitate the crystallization process of the zeolite and the nano-sized products were obtained. DD3R type zeolites have very small 8-ring with an aperture of 4.4 × 3.6 Å which enable only small molecules to adsorb. The adsorption isotherm for CO₂ was shown in figure 2(c). The sample was treated under vacuum and 473 K before adsorption experiment. When the partial pressure of CO₂ was increased to 1.0 bar, the CO₂ adsorbed amount was about 0.83 mmol g⁻¹. As shown in table 1, the synthesis of nanocrystalline DD3R needs very long time which implies more energy consumption [21]. If microwave assisting method was used, the synthesis time can be reduced greatly. However, the particle size is still relatively large [11]. In this work, we combine the character of microwave assisting and DGC method to optimize the synthesis process. It is found that the MADGC method has obvious advantage in decreasing of synthesis time and nanocrystals formation. When operated at same temperature, microwave energy will provide fast and homogeneous heating which contributes to the fast nucleation and crystallization [31].

3.2. Study of the microwave treated gel

In order to explore the mechanism of MADGC method, the microwave treated gel was tracked down. The powder XRD pattern and TEM image of the gel are showed in figures 3(a) and (b) respectively. The Bragg peak was clearly observed after 7 h microwave heating at 433 K. Although mostly amorphous, the characteristic peaks of Si-DD3R were already defined. Thus, some Si-DD3R structure units existed in the microwave treated gel. Combining with the TEM image, many lattice fringes were obviously detected which were marked by red circle in figure 3(b). It was seen that the crystal lattices directions in any of the crystal nuclei were different from each other, and the crystals were then probably grown outward from the dispersed nuclei progressively. This phenomenon expresses that some crystal nuclei are already existed in the microwave treated gel. Although most of nanoparticles are amorphous, they still existed as intermediates in the course of crystallization of zeolites Si-DD3R. The nano-scale transformations studied by TEM were coupled with a set of complementary analyses which provided an insight into the function of the microwave reaction. Microwave energy in this pre-synthesis process is quite significant. According to the previous reports, microwave heating can radically decrease the time for synthesis of nanoporous materials and can also give raise to the formation of the nanoscale products occur more uniformly [32, 33]. That implies the obvious improvement of the nucleation rate over the growth rate in the formation of initial crystallites. Microwave assisting has the advantage of decreasing synthesis time and particle size compared with the conventional synthesis method for Si-DD3R.

3.3. Effect of fluorine source on the synthesis of Si-DD3R type zeolites

Another key step for the formation of nano-sized Si-DD3R was the mixing medium of EDA and HF which made a sufficient dissolve of ADA and effectively avoided the separation of ADA in the synthesis procedure. Interestingly, if HF was substituted by KF (F⁻/Si = 1.2) and HCl was used to adjust the pH to about 9.5, the
nano-sized Si-DD3R zeolites cannot be obtained. In this case, the structures of the microwave treated gel marked KF-1 and the finial products marked KF-2 are confirmed by the powder XRD patterns (figure 4(a)). These diffraction peaks are associated with SGT structure. One probably reason for the existence of the by-product is

Figure 2. Powder XRD patterns of DD3R-type zeolite ((a): A, simulated; B, prepared), SEM image of prepared DD3R-type zeolite (b) and CO2 adsorption of prepared DD3R-type zeolite (c).
the change of pH and the formation of protonated ADA. The nucleation of SGT is easier than Si-DD3R, which is almost completely crystallized during the microwave pre-treated. The peaks intensity of KF-2 observed increase rapidly after the DGC process according with the increased sizes and the regular shape of KF-2 (see figures 4(b) and (c)). The benefits of the fluoride addition for the preparation of zeolites have been very often reported [34–36]. Differ from the other zeolites, fluoride is neither as a structure directing agent nor as a mineralizing agent in the Si-DD3R synthesis, that may because the non–cationic template carried. So far, the Si-DD3R zeolites have already been synthesized under the NH4F, HF and KF conditions [37], whereas, the alkaline fluoride sources could increase the alkalinity in EDA condition. In our case, the existence of HF enables a better

Table 1. Comparison of Si-DD3R crystals prepared by various methods (without seeding).

| Synthesis method | Synthesis time | Reaction temperature | Crystal size | References |
|------------------|----------------|----------------------|--------------|------------|
| HS               | 25 d           | 433 K                | 70–100 nm    | [21]       |
| HS               | 15 d           | 433 K                | ~100 μm      | [25]       |
| MS               | 3 d            | 433 K                | ~2 μm        | [11]       |
| MADGC            | 7 h            | 433 K                | 30 nm        | This work  |

HS: hydrothermal synthesis, MS: microwave aided synthesis.

Figure 3. Powder XRD pattern (a) and TEM image (b) of HF-1.

Figure 4. Powder XRD patterns (a) of samples (KF-1, microwave treated gel prepared with KF; KF-2, final product of zeolite prepared with KF) and SEM images of KF-1(b), microwave treated gel prepared with KF) and KF-2 (c), final product of zeolite prepared with KF).
solubilisation of ADA, suppresses the formation of lattice defects, adjusts the pH and creates a suitable environment for the framework crystallization.

4. Conclusions

In summary, the nano-sized Si-DD3R zeolite was synthesized by MADGC method with uniform particle size about 30 nm. From the synthesis result, it can be concluded that EDA and fluorine source are both beneficial for the dissolution of ADA. The EDA-KF system was examined and SGT type zeolites were obtained under this condition. So HF acts as both fluorine source and acid to adjust the pH. The microwave assisting in the process was important for nucleation and plenty nuclei formed in this process, which was favored to nano-sized zeolites crystallization and rapid synthesis of Si-DD3R. Following the DGC step, the uniform nano-sized Si-DD3R zeolites were successfully synthesized. The MADGC method showed obvious advantage in decreasing in situ synthesis time of Si-DD3R and the particle size compared with conventional synthesis method.

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