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Nanocrystalline zeolites in supercritical water. Part B: Challenges of synthesis in organotemplate-free condition

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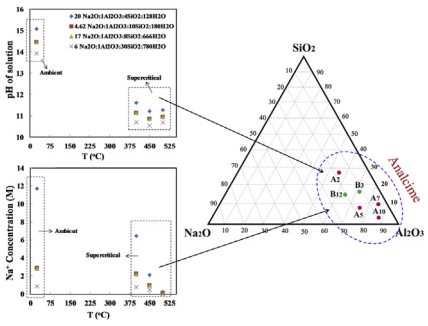
HIGHLIGHTS

- Applying single and two-step procedure for the rapid synthesis of nanocrystalline zeolites in SCW.
- Study on the effects of operational parameters in free-template condition.
- Rapid synthesis of zeolite W in SCW as valuable product.
- Study on the main reasons for the synthesis of analcime zeolite and other impurities.

GRAPHICAL ABSTRACT



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ABSTRACT

In the second part, fast synthesis of nanocrystalline zeolites in supercritical water (SCW) condition is studied in the absence of hazardous organic templates with a main product of analcime. The reason is attributed to the reduction in ion dissociation in SCW. In order to reach higher ion dissociation and therefore increase the chance to obtain other type of zeolites, first the alkalinity atmosphere of precursor batch composition changed from sodium hydroxide to potassium hydroxide in SCW followed by adding a long-chain alcohol (namely 2-decanol) in order to add the concentration of OH^- in synthesis system. The addition of 2-decanol shows a noteworthy modification in the size and size distribution of nanocrystals as well as product yield. This method is green and promising for the rapid synthesis of zeolitic nanoparticles in uniform size with a high degree of purity and crystallinity as well.

1. Introduction

The importance of aluminosilicate zeolites as catalysts [1–3] and adsorbents [4] in the industrial processes such as oil refining and fine chemicals production is undeniable since they possess outstanding thermal, hydrothermal stabilities, high surface area, large pore volume and uniform microporous channels [5]. Generally, zeolites are synthesized by the hydrothermal technique in the presence of toxic and costly organic templates and water in the sealed autoclaves under autogenous pressure [6,7]. Not only the cost of zeolite increases using expensive organic templates, but they results in the production of harmful by-products such as gases [8]. Also removing the polluted organic templates-water waste needs a post-process such as combustion at high temperature, which strongly influences the environment [9]. Since, using organic templates and solvents in the hydrothermal synthesis of zeolites is a key challenge, conse-

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quently, development of sustainable and environmentally friendly methods for the synthesis of zeolites has attracted much attention [10–14]. In this way, to overcome the disadvantages mentioned above, an organotemplate-free synthesis technique was effectively developed based on a seed-directed route for synthesizing aluminosilicate zeolites [15]. Here, by inducing zeolite seeds in the absence of any organic templates, the zeolite crystals are grown. However, this methodology gives relatively low zeolite yield due to a large amount of consumption of water as well as micro-size particles [16–19].

Here, SCW refers to the water at pressure and temperature above the critical point (SCW; T > 374 ° and P > 22.1 MPa) which is a newly-developing research topic in recent 30 years. SCW has many special properties, such as density close to the liquid, the ability to dissolve close to the liquid, viscosity and diffusion coefficient that is close to the gas, etc. Therefore, it has many advantages, such as fast mass transfer rate, density, dielectric constant, and so on [20]. Water in the supercritical state is different from general water in the structure; the properties also different with the change of temperature and pressure around the critical point [21,22]. SCW with a single-phase without surface tension, and no L/G phase boundary shows just as a organic solvent instead of it shows in the normal temperature [23]. The physical and transport properties of SCW are between gas and liquid. It has a lower dielectric constant, which can change the solubility of metal ions [24], and it also has weaker hydrogen bonds, so it can make many organic ingredients to get the miscibility. Since the relative permeability (ε) of the SCW is very small, it is helpful to maintain the nanostructure in the process of nanomaterial preparation where the aggregation problem must be solved [25]. These unique properties are beneficial to the synthesis of nanomaterials with controllable size and dispersion where all operating parameters (pH, temperature and pressure, the concentration of reactants, reaction residence time and so on) of SCW method can be adjusted that shows the method is flexible.

It also can adjust the component, particle size, and morphology of the end-product by changing the operating parameter (reaction temperature, pH, flow rates, morphology, and concentration of precursors) [25–31]. Further, the nanomaterials synthesized by the supercritical method have high purity and high crystallinity compared with the traditional methods. Furthermore, the supercritical method does not use an organic solvent, and the reaction time is short, so this method is regarded as environmentally friendly [20]. Due to the characteristics mentioned above of SCW, there is no doubt that there will be greater development space and broad application prospects in the field of nanomaterials synthesis. Rapid synthesis of different zeolites nanocrystals, namely LTA (A), FAU (X, Y), MFI (silicalite-1), ANA (analcime), as well as SAPO-34 and smectite nanoclay (montmorillonite) was carried out successfully in SCW only in 15–30 min, compared with 9 days in low-temperatures hydrothermal synthesis condition.

Although in the above-stated syntheses experiences in SCW, the zeolite product yield significantly increased, however, they still require the presence of toxic and expensive organic templates like tetra-methyl ammonium hydroxide (TMAOH), tetra-ethyl ammonium hydroxide (TEAOH), tetra-propyl ammonium hydroxide (TPAOH), and tetra-methyl ammonium bromide ($(CH_3)_4N(Br)$). These templates have a *structure-directing role* which is widely used to direct the hydrothermal synthesis towards the desired structure with the influence on controlling the morphology of synthesized crystals [8,9]. As a consequence, in current research, we have tried to examine the possibility of zeolite synthesis in the same reaction environment, but in organotemplate-free condition. Here, the effects of synthesis factors on the yield and product type of zeolite in SCW in the absence of organic templates were studied in detail. The effect of starting materials with different batch compositions, using NaOH and KOH as the alkaline sources as well as the operational conditions were carefully investigated. Further, the effect of long-chain alcohol (2-dodecanol) as OH-donor instead of the organic template was examined. By the help of our previous findings in the presence of toxic organic template [32–36], we also report the challenges of the zeolite synthesis in SCW without an organic template. The strategy for synthesizing zeolite X (FAU) and zeolite W nanocrystals, as the main valuable products were explained as well. As far as we know, this is the first report of the synthesis of analcime and zeolite W by this technique with kalsilite as a valuable mineral by-product.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, Merck Co., Ltd.), colloidal silica with trade name Ludox HS-30 (Sigma-Aldrich), aluminum isopropoxide (Merck Co., Ltd.) and water-glass (sodium silicate solution, 27% SiO_2, 8% Na_2O, Merck Co., Ltd.) were used as sources of silica. Sodium hydroxide (NaOH, Merck Co., Ltd.), potassium hydroxide (KOH, Merck Co., Ltd.), and sodium aluminate (54% Al_2O_3, 41% Na_2O, Merck Co., Ltd.) were utilized as the source of alkaline and alumina without further purification, respectively. 2-dodecanal ($CH_3(CH_2)_{10}CH_2OH$) with 99% purity was provided from Sigma-Aldrich.

2.2. Precursor preparation

Our previous investigation involves the details of the procedure for preparation of zeolite precursor in the presence of organic templates. Numerous effective operational parameters were studied extensively [32], and the optimized condition for the synthesis of the related zeolite nanocrystals was introduced. However, as mentioned before, the possibility of zeolite synthesis from the low-cost materials in the absence of organic template is investigated in the current study from the economic and environmental point of view. Here, the strategy for the zeolite precursor preparation was defined in two sections: In the first try (set A), the synthesis formula was extracted from the low temperature hydrothermal synthesis as applied for the large-scale production of zeolites [32] where crystallization temperature and duration, as well as aging time, were adjusted to 450 ° , 15 min, and 1 day respectively, according to the previous results obtained from the synthesis in the presence of an organic template [32]. The most difficulties of working with high temperature- pressure systems, especially small type autoclaves which were applied in the current research is installing the temperature- pressure transmitter in order to register the actual data of reactor inlet. For such case, we have expanded a MATLAB code which predicted the demanded time to reach equilibrium. In short, this code estimates the time required to reach the equilibrium temperature by taking into account the outer wall temperature of the reactor as the set point. The details of estimation is available in the appendix of ref [25]. However, the thickness of the reactor wall used in this study is less than 1 cm and the estimated time to reach equilibrium temperature is ignorable, for instance less than 1 min in case of T = 500 °C as the set-point final temperature. Table 1 shows the composition of precursor in which the silicon was supplied from various sources of silicon, *i.e.*, water glass (A_1, A_4, A_7, A_{10}), colloidal silica with trade name Ludox HS30 (A_2, A_5, A_8, A_{11}), and TEOS (A_3, A_6, A_9) respectively. Sodium aluminate was also selected as a source of alumina. For the preparation of the synthetic solution, first sodium aluminate was added to water with a specific amount of sodium hydroxide, and then the source of silicon was introduced by the simultaneous stirring of the solution with a magnet stirrer.