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EMT-type zeolite nanocrystals synthesized from rice husk

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ABSTRACT

Nanosized EMT-type zeolite crystals with a diameter of 15 nm are synthesized from a precursor suspension free of organic template using rice husk ashes (RHA) as a silica source. The crystallization process of the EMT-type zeolite is accomplished within 28 h at 28 °C. The fully crystalline EMT-type zeolite nanoparticles have equilateral hexagonal shape, Si/Al ratio of 1.28 and high crystalline yield of 75%.

1. Introduction

Rice husk (RH) is an agricultural by-product coming from rice production with high silica content (15–28 wt.%). The anticipated world rice production in 2012 is 489.1 million tons [1], which means that approximately 122–163 million tons of rice husk biomass was generated globally in 2012. Rice husk ash (RHA) is obtained when rice husk is combusted, and the resulted RHA consists of 85–98 wt.% silica. The purity of the RHA depends on the combustion conditions, rice variety, regional climate and geographical situations for rice cultivation [2].

Rice husk is usually not recommended as animal feed due to its low nutritional values and also is hardly digested by animals. Thus, the most common RH disposal methods are open field burning and landfilling, which result in energy waste, greenhouse gas emission, air pollution, and huge landfill space occupancy due to their low bulk density [3,4]. To address these issues, several processes for making full use of RHA were developed [5–9].

RHA can be used as a low-cost source of silica for production of silicon based materials with industrial and technological interests. Among these materials, molecular sieves (zeolites), which are silica-based, were prepared and reported by several groups [10,11]. Zeolites are hydrated porous crystalline aluminosilicates with open framework structures made up of tetrahedral SiO_4^{4-} and AlO_4^{3-} units. Zeolites are typically prepared by hydrothermal synthesis method starting from gels or suspensions containing silica, alumina, structure-directing agent (organic/inorganic) and water. Different sources of silica are applied to produce zeolites from the same precursor gel or suspensions. Depending on many variables during the crystallization, zeolites with various morphology, size and chemical composition are obtained [12]. Most of the silica sources used in the zeolite synthesis are commercially available in the form of sol, gel, fumed solid, or organic derivative as tetraethylorthosilicate [13].

Zeolites such as Na-A [14], faujasites [15], mordenite [16], ETS-10 [17], beta [13], K-L [18], ZSM-5 [19], ZSM-12 [20], ZSM-22 [21] and ZSM-48 [22] were synthesized from the RHA at temperatures above 90 °C. In some cases, harmful and costly organic templates were used to direct the formation of desired zeolite structures and to control the size of zeolite crystals [19,22]. Furthermore, nanosized zeolites derived from RHA were recently prepared at temperature above 60 °C (e.g. K-L [18], hydroxysodalite [23], Na-A [24], Na-X [24]). The physicochemical properties of the nanosized zeolites were modified by controlling their size and morphology, which have an important impact on their further applications [25–27].

Certain nanosized zeolites were synthesized at moderate temperatures (50–100 °C) to ensure nucleation and crystallization of desired zeolite phase with defined particle size and morphology. However, there is no paper reporting on the synthesis of zeolite nanocrystals at room temperature using rice husk ash as a silica source. Recently the preparation of template-free EMT zeolite from water glass at ambient conditions was reported [28,29]. Unlike its

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cubic FAU polymorph that has only supercages (1.15 nm^3), the EMT-type zeolite, has two cages: hypocage (0.61 nm^3) and hypercage (1.24 nm^3) due to different stacking of faujasite sheets, which creates unique catalytic and sorption properties of this material [30].

In this paper, the synthesis of nanosized EMT-type zeolite free of organic template at ambient conditions using rice husk agricultural waste as a silica source is presented. The silica from the rice husk ashes is extracted and characterized prior using for the synthesis of the EMT-type zeolite from the Na_2O–Al_2O_3–SiO_2–H_2O precursor suspension.

2. Experimental section

2.1. Preparation of silica precursor

Rice husk (RH), which was collected from a rice mill, was washed with water to remove dusts and mud. The clean RH was filtered and dried at 60 °C overnight. The clean RH was then treated with 1.5 M HNO_3 solution (1.5 L) under agitation (90 rpm, 15 h) to remove traces of other inorganic compounds. The RH was washed with distilled water until the pH of the rinsing solution reached ~7. Then the RH was dried at 60 °C overnight and calcined at 600 °C for 10 h (heating rate of 5 °C min^{-1}) to obtain white amorphous silica (RHA) as final product.

2.2. Synthesis of EMT-type zeolite nanocrystals

EMT-type zeolite was synthesized as follows: initially, solution A was prepared by dissolving RHA (6.00 g) and sodium hydroxide (25.58 g, Prolabo, 99%) in distilled water (31.16 g) at 100 °C for 2 h. Solution B was prepared by dissolving sodium aluminate (3.73 g, $NaAlO_2$, 53% Al_2O_3, 42.5% Na_2O Sigma–Aldrich), sodium hydroxide (1.00 g, Prolabo, 99%) in distilled water (46.74 g). Then Solution B was added slowly into Solution A under vigorous stirring to give a gel mixture with the following chemical composition: $5SiO_2$:$1Al_2O_3$:$18Na_2O$:$217H_2O$. The gel suspension was continuously stirred for 10 min, and then subjected to crystallization at 28 °C for 28 h. The crystallization was interrupted at various intervals, and the solids were extracted *via* high-speed centrifugation (20,000 rpm, 60 min) followed by re-dispersion in double distilled water; this procedure was repeated several times until the final colloidal suspensions reached pH of 7.5. Then the EMT-type zeolite suspensions were freeze-dried prior to characterization.

2.3. Characterization of EMT-type zeolite

The chemical compositions of the samples were determined by inductively coupled plasma optical emission spectroscopy (Varian *Vista MPX* ICP-OES). The crystallinity of the solids was analyzed with a PANalytical X'Pert PRO diffractometer with Cu K_α radiation (λ = 0.15418 nm, 40 mA, 45 kV, step size of 0.02° and a scan speed of 0.2°/min). The degree of crystallinity was calculated based on the count numbers of the three most intense diffraction peaks with the corresponding [*hkl*] values at 5.84 °2θ [1 0 0], 10.12 °2θ [1 1 0] and 31.13 °2θ [5 0 3] for each sample in relation with the reference EMT zeolite [31]. The size and morphology of the crystals were examined by a Philips XL-30 scanning electron microscope (SEM) and a FEI Titan 80–300 transmission electron microscope (TEM) with acceleration voltage of 30 kV and 300 kV, respectively. The size of the amorphous or crystalline single particles was determined by counting of 40 particles randomly during the TEM study in different sample regions.

The porosity of amorphous silica, semi-crystalline and crystalline EMT-type zeolite samples was determined by a Micrometrics ASAP 2010 nitrogen adsorption analyzer. The powders were first dehydrated at 200 °C under vacuum overnight prior to the measurement at −196 °C. The specific surface area was calculated using BET equation in the P/P^0 range of 0.05 and 0.30 (the BET constant values, *C*, of the samples are included in Table S1). The external surface area and the micropore volume were determined using a *t*-plot technique. The average micropore and mesopore diameters of the samples were estimated by Density Functional Theory (DFT) and Barrett–Joyner–Halenda (BJH) methods, respectively.

3. Results and discussion

3.1. Characterization of amorphous silica extracted from rice husk ash

The XRD pattern of the RHA contains a broad hump in the region of 15–30 °2θ indicating that amorphous silica has been obtained (Fig. S1). The amorphous RHA sample was subjected to N_2 sorption and SEM measurements and the results are shown in Figs. S2 and S3, respectively. The chemical composition and main properties of the amorphous silica are shown in Table 1. The amorphous RHA has a BET surface area of 135 m^2/g, and possesses a considerably high external surface area of 78 m^2/g. The BET and external surface area of the amorphous silica suggest that this source is appropriate for preparation of nanosized zeolites [32,33]. Besides, the high purity of the RHA is confirmed by the ICP-OES, i.e., the RHA contains 97.1% SiO_2, very small-unburned carbon impurities and negligible amount of iron (0.02%).

3.2. Synthesis of nanosized EMT-type zeolite

The synthesis of EMT-type zeolite nanocrystals was performed under mixing of transparent alumina and RHA silicate solutions. The alumina solution was added slowly under vigorously stirring to the RHA silicate solution in an ice water bath (highly exothermic reaction), resulting in the formation of aluminosilicate species in the precursor suspensions. The formation of amorphous precursor suspensions was found to have a great influence on the subsequent processes of nucleation, crystal growth of the metastable EMT-type zeolite. After mixing, a viscous suspension was formed immediately, which indicated that the polymerization process of the Si–Al species occurred resulting in the formation of particles with uniform size and morphology. The suspension became less viscous during the crystallization, and crystallization process was completed for 28 h. The final crystalline suspension is highly colloidal stable and no sedimentation occurred with time even in the non-purified samples.

The growth of EMT-zeolite nanocrystals in the precursor suspension was followed by XRD. The diffraction pattern of the

Table 1
Chemical composition and properties of amorphous silica extracted from rice husk ash.

Property	Silica from rice husk ash
Color	White
Crystalline nature	Amorphous
SiO_2 (%)	97.1
Al (%)	n.d.
Na (%)	n.d.
C (%)	0.31
H (%)	0.24
Fe (%)	0.02
BET surface area (m^2/g)	135
External surface area (m^2/g)	78
Average pore diameter (nm)	5.75
Total pore volume (cm^3/g)	0.21

n.d.: not detectable.