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Synthesis of colloidal stable Linde Type J (LTJ) zeolite nanocrystals from rice husk silica and their catalytic performance in Knoevenagel reaction

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HIGHLIGHTS

- Nanosized LTJ-type zeolite is hydrothermally synthesized from rice husk ash.
- LTJ nanozelites can be obtained by careful control the heating time.
- LTJ nanozelites (ca. 220 nm) are colloidally and thermally stable.
- The zeolite gives 88.9% conversion in Knoevenagel reaction within 2 h.
- The catalysts can be easily separated after reaction and are recyclable.

ABSTRACT

Nanoscaled aluminosilicate zeolite Linde J (structure code LTJ) was synthesized from rice husk ash (RHA) under hydrothermal condition. Structural phases, morphologies, crystal size and chemical compositions of the nanocrystals were characterized by XRD, IR, FESEM, TEM, ICP-OES, TG/DTG and DLS/zeta potential analyses. The XRD and Rietveld refinement studies revealed that pure LTJ-type zeolite (Si/Al ratio = 1.86) can be obtained from the precursor gel of 3.75SiO2·1Al2O3·15K2O·132H2O at 100 °C. The results also showed that co-crystallization of zeolite K–F could be avoided by extending the crystallization time to 30 h. The prepared zeolite nanocrystals (ca. 220 nm) exhibited long-term stability in colloidal form without adding any organic template. The zeolite framework structure was thermally stable up to 800 °C. The nanosized zeolite showed good catalytic performance in solvent-free Knoevenagel reaction, with ca. 88% reactant conversion and 100% product selectivity even after fourth cycle of reaction.

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1. Introduction

Zeolites are crystalline microporous aluminosilicates which are constructed from tetrahedral AlO4 and SiO4 units. The unique crystalline porous structure of zeolites yields valuable physico-chemical properties for cation exchange, molecular sieving, catalysis and adsorption. Today, zeolites are widely employed in industrial [1], environmental [2], biomedical [3] and intensive agriculture [4] applications.

In order to reduce the cost of zeolite synthesis, attempts have been made to use rice husk ash (RHA), an agriculture waste, as silica precursor in zeolite synthesis. In fact, various types of zeolite can be prepared using RHA, these including NaA [5], faujasite-X [6], mordenite [7], ETS-10 [8], Beta [9], ZSM-5 [10], ZSM-12 [11] and ZSM-48 [12] zeolites. However, only a few types of zeolite have been successfully synthesized in nanometer scale (<100 nm with at least one dimension is considered [13]) from RHA (e.g. KL [14], hydroxysodalite [15], NaA [16], faujasite-X [16], and EMT [17]). Thus, the synthesis of nanosized zeolite from this cheap and
renewable silica precursor is worth to be explored further.

On the other hand, remarkable advanced applications related to small pore zeolites catalysis and gas separation [18]. According to the International Zeolite Association (IZA), zeolites with pore openings limited by 8 atoms in tetrahedral coordination are defined as “small pore zeolites”. Linde Type J (LTJ) zeolite which has zigzag 8–ring channels intersections giving a 2-D pore system with a pore diameter of 3.12 Å [19] is considered one of the small pore zeolites. Despite it was first discovered by Breck and Acara in 1961 [20], the first complete structure description was solved only in 2011 [21]. Furthermore, there are very limited papers reporting on the synthesis and application of LTJ zeolite considering its low synthesis reproducibility due to co-crystallization of other zeolite phases [21]. In order to explore the potential of LTJ zeolite in advanced applications, the preparation of pure LTJ zeolite is of the utmost importance.

Herein, we report a facile hydrothermal synthesis of LTJ-type zeolite from RHA. It is worth to mention here that the resulting synthesized zeolite was found to be in the nanometer size. By carefully controlling the crystallization time, pure LTJ zeolites can be easily obtained. More strikingly, the colloidal suspension of the zeolite was stable without using any organic template. Such property is beneficial for many new applications including thin film deposition [22], membrane fabrication [23] and molecular sieves for desalination, water, gas and ion separations [24,25]. The potential of the nanosized LTJ zeolites as solid base catalyst in Knoevenagel reaction has also been demonstrated.

2. Experimental

2.1. Materials and synthesis of LTJ zeolite nanocrystals

High purity of RHA (97.6% SiO₂) was first prepared according to reported method [14]. Typically, rice husk was initially washed with water to remove dust and mud. The rice husk was immersed in 1.5 M HNO₃ and shaken for 15 h at 90 rpm. The acidified rice husk was then washed with distilled water until the pH of rice husk reached 7.0. The rice husk was then burnt in a muffine furnace maintained at 600 °C for 10 h to obtain white amorphous RHA powder (98% SiO₂) as the final product.

A clear silicate solution was then prepared by dissolving KOH pellet (19.38 g, 85%, Merck) and the RHA (3.000 g) in distilled water (10.85 g) at 100 °C for 2 h under continuous stirring. A clear aluminate solution was prepared by mixing aluminum hydroxide (1.95 g, 99.9%, Acros) and KOH pellet (6.46 g) in distilled water (16.28 g) followed by stirring at 100 °C for 14 h. Both solutions were cooled to room temperature. To avoid gelation, the silicate solution was added slowly into the aluminate solution under vigorous stirring. The sol with a final composition of 3.75SiO₂·1Al₂O₃·15-K₂O·132H₂O was stirred for an additional 10 min prior to crystallization at 100 °C for 30 h. The solid products were then purified with distilled water and freeze-dried.

2.2. Characterization

The powder X-ray diffraction (PXRD) patterns were recorded with Bruker D8 diffractometer (Transmission Mode) with Cu-Kα radiation (λ = 1.5406 Å). Rietveld refinement was done using GSAS software. Transmission electron microscopy (TEM) analysis was performed with a Philips CM12 electron microscope operated at 200 kV. Scanning electron micrographs were taken on a JEOL JSM-6701F field-emission scanning electron microscope (FESEM). The chemical composition of RHA and zeolite were determined by using inductively coupled plasma optical emission spectroscopy (Varian Vista MPX ICP-OES). Prior to analysis, 0.05 g of the solid sample was dissolved in an aqua regia solution composed of 6HF:2HNO₃:2HCl:1H₃BO₃. The infrared spectrum was recorded on a Perkin Elmer Spectrum One spectrometer using KBr pellet technique (KBr: sample ratio = 200:1). Dynamic light scattering (DLS) and zeta potential (ζ) analyses were measured by a Malvern ZetavSizer Nano Series equipment. Solid-state 29Si MAS NMR spectrum was recorded using a Bruker Ultrashield 300 spectrometer with tetramethylsilane, TMS, as the reference standard. The measurement was carried out at 79.4 MHz and single-contact cross-polarization pulse program was used. The spectrum was obtained with a pulse length of 2.7 μs, a repetition time of 6 s and a contact time of 4 ms. The porosity analysis was performed using a Micromeritics ASAP 2010 instrument. The powders (ca. 50 mg) were first dehydrated at 300 °C under vacuum overnight prior to the measurement at −196 °C. The external surface area was calculated using t-pplot equation.

2.3. Catalytic experiments

Solvent-free Knoevenagel reaction was conducted as follows: LTJ zeolite (0.22 g), benzaldehyde (11 mmol, 99%, Merck) and ethyl cyanoacetate (11 mmol, 99%, Merck) were added into a 15 mL Teflon container. The Teflon container was autoclaved and magnetically stirred in an oil bath at 80 °C for 2 h. The reaction solution was withdrawn and analyzed using a gas chromatograph (Hewlett-Packard 5880) equipped with a Carbowax Equity 1 non-polar capillary column. The identity of the product was confirmed by a GC–MS (Perkin–Elmer GC–MS 2000 system). The reusability study of zeolite catalyst was carried out as follows: LTJ zeolite solid was separated after the first Knoevenagel reaction run, further washed with diethyl ether and finally dried (100 °C, 2 h) before use for the three subsequent cycles of catalytic reaction. After the reaction, the reaction solution was again separated and analyzed using GC.

3. Results and discussion

3.1. Synthesis and characterization of LTJ zeolite

Small pore LTJ zeolite was hydrothermally synthesized using RHA. In previous work, LTJ was usually obtained with a substantial zeolite K–F impurity [21]. In this study, co-crystallization of zeolite K–F together with Linde J was also observed when the synthesis

![Fig. 1. XRD patterns of the samples after hydrothermally heated for (a) 18 h and (b) 30 h. * indicates the presence of K–F zeolite phase.](image-url)
precursor was hydrothermally heated for 18 h (Fig. 1a). However, with heating time prolonged to 30 h, the reflections due to zeolite K–F phase (2θ = 13.51°, 25.53°, 28.94°, 31.84°, 40.11°) disappeared completely and pure LTJ-type zeolite phase was obtained (Fig. 1b). This indicates that zeolite K–F is a metastable phase and its presence in the reaction product of LTJ zeolite can be reduced by employing longer hydrothermal crystallization time. Furthermore, the crystallization time was also extended to 96 h and no competing zeolite phase was observed in the solid product (See Supporting Information: Fig. S1). Thus, this zeolite synthesis is promising when working in the reported preparation conditions and chemical concentrations (see Fig. 2).

The PXRD pattern of LTJ-type zeolite synthesized from RHA was indexed using the TREOR autoindexing program [26]. The final Rietveld refinement gave the following data: orthorhombic space group P2₁2₁2₁ with a = 9.5868 (14) Å, b = 9.9068 (15) Å, c = 9.5084 (15) Å, α = β = γ = 90° and V = 903.0 (4) Å³. The crystallographic data of the LTJ nanozeolites are listed in Table 1 and are compared to those of previous work [21]. Furthermore, there is a good qualitative agreement between the experimental PXRD pattern and the calculated XRD pattern obtained from simulation. Profile fitting using Rietveld refinement method gave good quality fit, indicating that the refined structure is correct and the LTJ phase nanozeolites are very pure. According to the ICP-OES elemental analysis, the Si/Al ratio of synthesized LTJ-type zeolite was 1.86, which was higher than the reported value (Si/Al ratio = 1) [21]. Furthermore, the Si/Al ratio was fully in accordance with the empirical formula of LTJ zeolite [K₂₋ₓ]·[Si₃₋ₓAlₓO₈]·yH₂O, where yH₂O is the amount of water adsorbed.

Table 1

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*Reference [21].

The FESEM image of LTJ nanozeolite is displayed in Fig. 3a. As shown, the nanocrystals had narrow particle size distribution and they were discrete and not agglomerated (Fig. 3a). The HRTEM showed a rectangular cuboid with rounded corners. The microscopic study revealed that LTJ nanocrystals were sized from 71 nm to 410 nm having a mean crystallite size of ca. 179 nm. In addition, the size of LTJ nanocrystals were 80 nm–450 nm with an average hydrodynamic size of ca. 220 nm according to the DLS result (Fig. 3c).

Stabilizing zeolite nanoparticles in colloidal suspension is an important task in film coating and membrane fabrication procedures. Usually, organic quaternary ammonium templates (e.g. TMAOH, TEAOH, TPAOH) are also employed as colloidal-stabilizers to stabilize nanozeolites in aqueous colloidal dispersions. Interestingly, the LTJ zeolite nanocrystals prepared were stable in water/ethanol solution (90:10 v/v) without the need of organic template (inset of Fig. 3c), giving a ζ-potential of ~30.1 mV.

The FTIR spectrum of the RHA-synthesized LTJ nanozeolite is shown in Fig. 3d. The bending vibration of T оч (T = Si, Al) is shown at 425 cm⁻¹. The absorption band at 558 cm⁻¹ is characteristic of zigzag 8-membered ring subunits present in LTJ zeolite. The vibration bands at 659, 695 and 760 cm⁻¹ can be assigned to the symmetric stretch of O–T–O [27]. The three bands at 986, 1036 and 1083 cm⁻¹ are assigned to the internal vibrations of Si–O–T asymmetric stretching mode [14]. The thermal stability of as-synthesized LTJ zeolite nanocrystals was also evaluated using TG/DTA analysis (See Supporting Information: Fig. S2). TG curve of LTJ zeolite nanoparticles shows that about 11% mass losses up to 250 °C, which is attributed to the desorption of water [28]. In addition, the DTG curve of LTJ zeolite shows a broad and intense endothermic signal at 145 °C. This signal was due to the energy received by the adsorbed water molecule to overcome the adsorption energy from the surface of zeolite. No significant weight loss and no DTG signal were detected from 300 to 800 °C indicating no structural collapse or phase transformation occurred up to 800 °C (Fig. S2). This observation was further confirmed by XRD and FTIR analyses where the XRD (Fig. 4A) and IR spectra (Fig. 4B) of LTJ-type zeolite nanocrystals remained intact after heating at 500 °C and 800 °C.

The 29Si MAS NMR spectrum of LTJ zeolite nanoparticles is also recorded (Fig. 5). It is shown that three peaks are detected at ~85.1 ppm, ~88.7 ppm and ~91.8 ppm in the zeolite sample after 30 h of hydrothermal treatment. The first intense peak at ~85.1 ppm is attributed to Si(4Al) coordinated species. As shown, the peak is narrow indicating that LTJ zeolite nanocrystals with identical chemical environment has been fully formed. Furthermore, the small peaks at ~88.7 ppm and ~91.8 ppm are assigned to Si(3Al), and Si(2Al) coordinated species. No peak was observed at around ~83 ppm, indicating that the zeolite sample has no
amorphous phase and this observation is fully in line with the data of XRD analysis [29].

The N₂ sorption isotherm of the LTJ-type zeolite nanocrystals is shown in Fig. 6. The nanocrystalline LTJ-type zeolite exhibited Type
IV adsorption behavior with type H3 hysteresis loop, which indicates the capillary condensation in open slit-shaped mesopores [30]. Type I isotherm which is usually observed for zeolites at low P/Po, however, was not observed in this study due to the smaller pore size of LTJ-type zeolite (σ = 3.12 Å) than the size of N2 probe molecule (σ = 3.64 Å) [31]. As a result, an external surface area of 22 m²/g and a total pore volume of 0.12 cm³/g were measured. On the other hand, the micropore volume and micropore surface area are negligible since the BET surface area is almost not measurable due to smaller pore size of LTJ zeolite than the molecular size of N2. Such phenomenon was also observed in hydroxysodalite small-pore zeolite system where only 5 m²/g of micropore surface area and 28 m²/g of external surface area were measured using N2 adsorption isotherm method [32]. Nevertheless, it was worthy of note that, although N2 was not able to probe this zeolite, this small pore nanozeolite can have potential applications in hydrogen molecule (σ = 2.89 Å) or helium (σ = 2.60 Å) separation, hydrogen storage, semiconductors and chromophore occlusion. Comprehensive work on LTJ-type zeolite in this aspect is in progress.

3.2. Catalytic activity and catalyst reusability

Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate was selected as model reaction to study the potential of LTJ zeolite nanoocrystals as a solid base catalyst. High conversion rate of 88.9% with ethyl 2-cyano-3-phenylacrylate as the only product was achieved within 2 h in the presence of LTJ nanozeolite (Fig. 7b). Without zeolite catalyst, Knoevenagel reaction still occurred but with a much lower conversion rate (17.9% after 2 h) (Fig. 7a). Thus, this study revealed that the oxygen atoms of the zeolite framework located at the external surface of LTJ zeolite, whose negative density charge are compensated by electropositive K⁺ cation, was catalytically active in this reaction.

The catalytic performance of LTJ zeolite was also compared with those of large pore zeolites containing various cations. It was shown that under autogenic pressure, small-pore LTJ zeolite nanoocrystals with accessible external surface had better catalytic performance (conversion = 88.9%) than H-β (15%) [33], H-Y (2%) [33], Zn-β (21%) [33], Zn-Y (9%) [33], Na-X (47%) [34], Li-ETS (44.3%) [35], K-ETS (31.5%) [35], Rb-ETS (33.3%) [35], Cs-ETS (32.7%) [35] and non-porous magnesia (78.2%) [35] that were applied in reflux condition.

Catalyst reusability is a major problem for solid catalysts in liquid phase reaction. Therefore, a reusability test for LTJ nanozeolites was thus carried out. The reactivity of the recovered zeolite nanocrystals was preserved after the second, third and fourth runs (conversion ca. 88% and selectivity to ethyl 2-cyano-3-phenylacrylate = 100%) (Fig. 8). The results suggested that the external surface of K-LTJ zeolite framework remained catalytically active to the Knoevenagel reaction even after several reaction cycles. Thus, this indicates that K-LTJ zeolite can be used as a potential solid base catalyst besides its potential molecular sieving applications.

4. Conclusion

In conclusion, nanocrystalline LTJ-type zeolite (ca. 220 nm) has been successfully synthesized using RHA. The results showed that the phase contamination by K-F zeolite can be suppressed by prolonging the crystallization time and hence highly pure LTJ-type zeolite can be obtained. The RHA synthesized zeolite nanocrystals were also colloidally stable without utilizing harmful and expensive organic templates. From an environmental perspective, this synthesis is extremely beneficial as it can be used to prepare pure nanosized molecular sieves in an eco-friendly way by using agricultural biomass. The K-LTJ zeolite can also be used as a potential solid base catalyst besides its potential molecular sieving applications.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.matchemphys.2015.01.061.

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