EMT-type Zeolite Nanocrystals Synthesized From Rice Husk

Eng-Poh Ng, Dr.
EMT-type zeolite nanocrystals synthesized from rice husk

Eng-Poh Ng a,⇑,1, Hussein Awala b,1, Kok-Hou Tan a, Farook Adam a, Richard Retoux c, Svetlana Mintova b,⇑

a School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
b Laboratoire Catalyse & Spectrochimie, CNRS-ENSICAEN, Université de Caen, France
c CRISMAT, University of Caen, 6, Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Article info
Article history:
Received 8 September 2014
Received in revised form 17 November 2014
Accepted 18 November 2014
Available online 27 November 2014

Keywords:
EMT
Nanozeolite
Rice husk ash
Room temperature synthesis

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%.

© 2014 Elsevier Inc. All rights reserved.

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 SiO4 4− and AlO4 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
cubic FAU polymorph that has only supercages (1.15 nm$^3$), the EMT-type zeolite, has two cages: hypcage (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$_2$O–Al$_2$O$_3$–SiO$_2$–H$_2$O 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$_2$O$_3$, 42.5% NaO 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$_2$O$_3$:18Na$_2$O:0.217H$_2$O. 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 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$_\alpha$ radiation ($\lambda = 0.15418$ 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 [100], 10.12 2θ [110] and 31.13 2θ [503] for each sample in relation with the reference EMT zeolite [31]. The size and morphology of the crystals were examined by a Philips XL-60 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, 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 Na$_2$ 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>
<thead>
<tr>
<th>Property</th>
<th>Silica from rice husk ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White</td>
</tr>
<tr>
<td>Crystalline nature</td>
<td>Amorphous</td>
</tr>
<tr>
<td>SiO$_2$ (%)</td>
<td>97.1</td>
</tr>
<tr>
<td>Al (%)</td>
<td>n.d.</td>
</tr>
<tr>
<td>Na (%)</td>
<td>n.d.</td>
</tr>
<tr>
<td>C (%)</td>
<td>0.31</td>
</tr>
<tr>
<td>H (%)</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>0.02</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>135</td>
</tr>
<tr>
<td>External surface area (m$^2$/g)</td>
<td>78</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>5.75</td>
</tr>
<tr>
<td>Total pore volume (cm$^3$/g)</td>
<td>0.21</td>
</tr>
</tbody>
</table>

n.d.: not detectable.
sample extracted after 5 min contains a broad peak in the range 25–33 °2θ, which is typical for amorphous aluminosilicate (Fig. 1a). This result is consistent with the SEM analyses where shapeless amorphous grains with a size of ca. 13 nm exist, which tend to agglomerate in larger units with a diameter of ca. 125 nm (Fig. S3). Furthermore, it can be seen that the isomeric particles about 10 nm are embedded in the bigger bodies with random shapes and morphologies (Fig. 2a). The content of amorphous solid particles separated from the suspension after 5 min treatment at 28 °C is about 47 wt.% (Table 2). The mass of the extracted solid after 10 h dropped to 42 wt.% and this solid is still amorphous according to the XRD observation. However the baseline, position and intensity of the amorphous hump increased in the XRD pattern indicating that structure re-arrangement of the material via condensation of –OH bonds probably occur under prolonged hydrothermal treatment [34]. Furthermore, the solid material extracted after 10 h synthesis has a Si/Al ratio of 1.41, which is a little lower than of the initial suspension, i.e. Si/Al ratio of 1.45 (Table 2 and Fig. 3). In this stage, the TEM pictures reveal the presence of particles with diverse shapes (Fig. 2b).

An abrupt increase in the solid yield (67 wt.%) is measured after 18 h of synthesis, and the XRD pattern of this sample shows the appearance of a diffraction peak at 6.0 °2θ, which is corresponding to [100] plane of the EMT crystalline phase (Table 2 and Fig. 1c). This indicates that the EMT zeolite crystals formed in the sample after 18 h (Table 2 and Fig. 1c). As can be seen, the Bragg peak is broad, and thus revealing the small size of the crystalline particles [35]. The relative crystallinity of the samples was calculated (see Section 2.3) and depicted in Fig. 3. These results indicate that 20% of crystallinity is achieved after 18 h of treatment. Although the TEM micrographs do not contain crystals with lattice fringes, some particles are completely amorphous but with hexagonal shape, and the size is comparable with the crystalline EMT particles. The size of the crystals in the sample treated for 24 h is about 10–19 nm, and these crystals do not change significantly further due to low crystallization kinetics at ambient temperature. The EMT zeolite crystals have lower Si/Al ratio (1.29) in comparison to the previous amorphous or semi-crystalline samples, and the chemical composition remains unchanged under prolonged crystallization period. After 28 h, fully crystalline EMT zeolite nanocrystals are obtained (Fig. 1e). As shown in the TEM image, all the amorphous entities have transformed into crystalline EMT particles while the size of crystals remains intact.

The evolution of the crystalline EMT-type zeolite from the amorphous solid involves not only changes in the chemical composition and morphology, but also changes in their porosity. The adsorption–desorption isotherm of the sample after 5 min exhibits Type III isotherm, typical of non-porous materials (Fig. 4a) [27]. The hysteresis loop at high partial pressure (P/P0) around 0.8–1.0 reveals the presence of textural mesoporosity. The external surface area of this sample is 78 m²/g, which suggests the presence of nanometer sized amorphous particles. When the hydrothermal treatment is extended to 10 h, the solid exhibits a small increase in the external surface area (80 m²/g) (Fig. 4b and Table 2). No change in the micropore volume is observed, which suggests that the EMT-type microporous network is not yet constructed. After 18 h of treatment, a small N2 uptake at low P/P0 couple with an increase of the BET surface area (140 m²/g) is detected, which is the first evidence for the formation of the EMT-type zeolite (Fig. 4c and Table 2). As shown, the total pore volume increased from 0.38 cm³/g to 0.57 cm³/g owing to the formation of microporosity and meso(textural)-porosity in the sample. With prolongation of the synthesis time to 24 h, an abrupt increase in the external surface area (205 m²/g), micropore volume (0.17 cm³/g) and total pore volume of 1.84 cm³/g is measured (Fig. 4d and Table 2).

Fully crystalline EMT-type zeolite is obtained after 28 h. At this stage, the amorphous entities are fully converted into EMT-type crystalline phase as shown by XRD, TEM and N2 sorption analyses (Figs. 1, 2 and 4). The EMT-type nanocrystals with a narrow particle size distribution (diameter of ca. 15 nm) are shown in the TEM pictures (Fig. 2). The N2 sorption isotherm is a combination of Type I and Type IV, due to the presence of micro- and textural mesoporosity (Fig. 4e). A large hysteresis loop is measured at high relative pressure, which can be explained by the presence of regular mesopores with a diameter of 22 nm, which are resulting from the packing of the EMT zeolite nanocrystals (Table 2). High BET surface area (590 m²/g) and high total pore volume due to secondary porosity of this solid giving a value of 1.45 cm³/g is recorded. Further hydrothermal treatment of the sample up to 48 h resulted in the phase transformation and decrease in the crystallinity of EMT-type zeolite (Fig. 3). Nevertheless, the Si/Al ratio of the solid sample remains intact. As can be seen in Fig. 2f, several new diffraction peaks at 14.13 °2θ [110], 24.68 °2θ [211], 32.00 °2θ [310], 35.08 °2θ [222] appear, which are attributed to the crystallization of high framework density phase (hydroxysodalite) [31]. The peaks are broad, thus indicating the small size and low degree of periodicity of hydroxysodalite nanocrystals. This result suggests that the EMT-type zeolite is the first kinetic and metastable phase forming in the precursor system; a conversion into more thermodynamically stable hydroxysodalite (SOD) phase after longer time is observed [36]. The hydroxysodalite, however, is not detected in the TEM images due to the trace quantity in the sample. Nevertheless, the TEM study reveals that the EMT crystals change slightly the shape from equilateral-hexagonal to elongate-hexagonal (Fig. 2f).

The phase transformation from EMT to hydroxysodalite is confirmed by a decrease in the microporosity of the samples (Fig. 4). As shown in Table 2 and Fig. 4f, the sample treated for 48 h has a BET surface area of 470 m²/g and a micropore volume of
The N$_2$ probe molecule (0.36 nm) is too big to diffuse inside the hydroxysodalite (0.25 nm), and hence reduced micro-pore volume is measured [37,38].

The transformation of amorphous aluminosilicates into EMT-type zeolite is further monitored by infrared spectroscopy using the structural fingerprint region of 400–1400 cm$^{-1}$. The IR spectra (Fig. 5a) show a broad band of asymmetric stretching of T–O–T bond (T = Si, Al) in the 900–1200 cm$^{-1}$ region. The band at 860 cm$^{-1}$ is due to silanol (Si-OH) bending mode, which is associated with silicon atom linked with the hydroxyl group in the framework and corresponds to the defect sites in the structure [39]. No significant changes in the IR spectrum are observed after 10 h of crystallization (Fig. 5b). After 18 h of crystallization, the beginning of phase transformation from amorphous into crystalline material is observed, which is in a good agreement with the XRD and N$_2$ results (Figs. 1c and 4c). The bands at 561, 671 and 744 cm$^{-1}$ correspond to the double-6-ring species (D6R) which are the secondary building units of the EMT-type structure and vibration of T–O–T symmetric stretching mode start to appear (Fig. 5c). These bands become more resolved after 24 and 28 h of

Table 2
Properties of samples prepared at 28 °C for different crystallization times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield $^a$ (wt.%)</th>
<th>Si/Al ratio</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>$d_{\text{micro}}$ (nm)</th>
<th>$S_{\text{ext}}$ (m$^2$/g)</th>
<th>$V_{\text{meso}}$ (cm$^3$/g)</th>
<th>$d_{\text{meso}}$ (nm)</th>
<th>$V_{\text{total}}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>47</td>
<td>1.45</td>
<td>78</td>
<td>0.00</td>
<td>0.77</td>
<td>78</td>
<td>0.27</td>
<td>18</td>
<td>0.27</td>
</tr>
<tr>
<td>10 h</td>
<td>42</td>
<td>1.41</td>
<td>80</td>
<td>0.00</td>
<td>0.77</td>
<td>80</td>
<td>0.38</td>
<td>22</td>
<td>0.38</td>
</tr>
<tr>
<td>18 h</td>
<td>67</td>
<td>1.35</td>
<td>140</td>
<td>0.02</td>
<td>0.73</td>
<td>100</td>
<td>0.85</td>
<td>32</td>
<td>0.87</td>
</tr>
<tr>
<td>24 h</td>
<td>76</td>
<td>1.29</td>
<td>510</td>
<td>0.17</td>
<td>0.73</td>
<td>205</td>
<td>1.67</td>
<td>35</td>
<td>1.84</td>
</tr>
<tr>
<td>28 h</td>
<td>75</td>
<td>1.27</td>
<td>590</td>
<td>0.19</td>
<td>0.74</td>
<td>250</td>
<td>1.26</td>
<td>22</td>
<td>1.45</td>
</tr>
<tr>
<td>48 h</td>
<td>74</td>
<td>1.28</td>
<td>470</td>
<td>0.15</td>
<td>0.73</td>
<td>190</td>
<td>0.97</td>
<td>25</td>
<td>1.13</td>
</tr>
</tbody>
</table>

$S_{BET}$: specific surface area, $V_{\text{micro}}$: micropore volume, $S_{\text{ext}}$: external surface area, $V_{\text{meso}}$: mesopore volume, $d_{\text{micro}}$: micropore diameter, $d_{\text{meso}}$: mesopore diameter.

$^a$ Calculated according to the amount of RHA used.
$^b$ Determined by DFT method.
$^c$ Determined by BJH method.
4. Conclusions

In conclusion, the synthesis of nanosized EMT-type zeolite at 28 °C using rice husk agricultural waste as silica source is reported. The analyses reveal that the EMT-type nanocrystals can be obtained after 28 h hydrothermal treatment of aluminosilicate suspensions without using harmful organic SDA. The transformation of the amorphous silica from RHA into crystalline EMT-type zeolite takes place by dissolution of the silica in the highly basic media, followed by crystallization of the metastable EMT-type zeolite and transformation into dense hydroxy sodalite under prolonged crystallization time. The highly crystalline EMT-type nanocrystals have diameter of 15 nm and a narrow particle size distribution. The synthesis reported in this work is extremely beneficial since large pore molecular sieve (EMT-type zeolite) with narrow crystal size distribution and high crystalline yield (75 wt.%) is obtained only for 28 h using agricultural by-product (RHA) as a silica source.

Acknowledgments

The financial support from Bio-Asia Program, RUI grant (1001/ PKIMIA/811264) and ANR TARGED is acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.11.017.