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Crystal growth study of K-F nanozeolite and its catalytic behavior in Aldol condensation of benzaldehyde and heptanal enhanced by microwave heating

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HIGHLIGHTS
- K-F nanozeolites are prepared in SDA-free system under microwave radiation.
- The nucleation and crystallization of nanozeolites are monitored and studied.
- The nanocrystals are formed after 2 min onwards at 100 °C.
- The crystals (ca. 39 nm, Si/Al = 1.26) have flattened cuboid shape morphology.
- The nanozeolite catalyze Aldol condensation of benzaldehyde and heptanal.

ABSTRACT
An investigation of nanosized potassium aluminosilicate F-type zeolite (K-F, structure code EDI) converted from rice husk ash (RHA) is reported. The crystallization process was studied in an organic template-free system under microwave radiation at 100 °C and the evolution was followed by spectroscopy and microscopy techniques. The study indicated that the crystallization rate of K-F zeolite was significantly enhanced using microwave radiation. The zeolite started to nucleate at 0.5 min and flattened cuboid shaped K-F zeolite crystals (ca. 39 nm, Si/Al = 1.26) were formed after 2 min onwards. The nanocrystalline K-F zeolite exhibited good catalytic performance in solvent-free Aldol condensation reaction between benzaldehyde and heptanal, with ca. 75% reactant conversion and ca. 67% jasminaldehyde selectivity even after fifth cycle of reaction.

1. Introduction
Zeolites are crystalline aluminosilicate microporous materials with open three dimensional framework structures. Zeolites are
widely used as adsorbents, ion exchangers and catalysts because of their uniform intracrystalline channels which are comparable to the molecular dimensions (typically between 2 and 10 Å) [1]. Particularly, zeolite crystals with crystallite size below 100 nm have receiving tremendous scientific interest due to their unique properties [2]. Zeolite nanocrystals have very low toxicity and hence they have been used in chemical sensing [3], semiconductors [4], drug delivery [5] and biomedicine [6,7]. Furthermore, nanocrystalline zeolites possess unique surface chemistry, diverse morphology, fast diffusivity, high thermal stability, high external surface area and large micropore volume where these excellent properties are important for the design of optical devices [8], catalysts [9] and energy storage [10]. In addition, functionalization and colloidal stabilization of zeolite nanoparticles also opens up the possibility of using these nanomaterials in many areas [11–13].

Zeolite nanocrystals with narrow particle size distribution are generally obtained from clear precursor suspension. Organic templates such as amines and/or tetraalkylammonium hydroxides in high amount are usually added in order to achieve a so-called supersaturation condition [14,15]. The crystallization process is then allowed to take place at moderate temperature for several days, producing nanocrystalline particles with high colloidal stability. So far, a number of zeolites (LTA, MFI, MEL, FAU, BEA) and zeotype (AFI, AEI, AFO, CHA, AEL) nanocrystals have been successfully synthesized using this approach [8,16–18]. This traditional synthesis, however, is not economically viable and harmful due to the large consumption of expensive organic templates, long crystallization duration and low crystalline yield (<10%). In addition, in order to open the pores of zeolites, the organic templates have to be decomposed and removed via high-temperature calcination (>500 °C), which further makes this synthesis approach to be industrially unfavorable [19–21].

Recently, many new synthesis approaches for the preparation of nanocrystalline zeolites have been proposed in an attempt to replace the existing organo-templating method. For example microchannel-assisting [22], microwave-assisting [23,24], centrifugation-assisted grinding [25], ionothermal [26], confined space [27], reverse microemulsion [28,29], and direct-conversion [30] syntheses. Nanosized zeolites prepared using organic wastes such as rice husk ash (RHA) from the system free of any organic template are also a promising approach [17,31]. It is because RHA contains 96–98% of pure amorphous SiO2 and it is cheap [32,33]. It has hence provided a green source of active silica for preparing many types of micro-mesoporous solids materials [34–39]. However, there are only several articles reported on the synthesis of nanocrystalline zeolites (e.g. A [40], X [41], Y [41], beta [33], ZSM-5 [42], LTL [43], LT [17], EMT [31]) using RHA under conventional heating.

Linde Type F zeolite or so-called K-F zeolite is a synthetic EDS-type analogue and its framework structure consists of interconnection chains of T5O10 tetrahedra (T = Si or Al) [44]. This type of zeolite has three-dimensional pores with two different types of 8-membered ring channel systems interconnected (diameter of 2.8 × 3.8 Å2 and 2.0 × 3.1 Å2) [44]. Zeolite K-F has been used in many applications such as in waste-water cleaning [45], gas separation [46], and soil amendment [47] due to its high affinity towards ammonium cations (NH4+). The synthesis of micrometer-sized K-F zeolites (>2 µm) was recently reported by using various precursor suspensions such as Li2O–Al2O3–SiO2–H2O [48], Li2O–BaO–Al2O3–SiO2–H2O [49], Li2O–Rb2O–Al2O3–SiO2–H2O [50], Li2O–Cs2O–Al2O3–SiO2–H2O [50,51], and TMA)O2–Li2O–Al2O3–SiO2–H2O [51]. The preparation of pure nanosized EDS-type zeolite (<100 nm) in organo-template free system, however, has not yet successful due to the difficulty to find proper synthesis formulations for crystallizing the nanosized material. Hence, an attention on this aspect is of utmost importance and is worth to be further investigated.

This paper describes the microscopic investigation of the formation of nanosized K-F zeolite using RHA as the reactive silica source. The crystals are grown in a hydrogel free of organic template where the entire crystallization process is conducted under dynamic condition and assisted with microwave heating. The potential of the nanosized K-F zeolites as solid base catalyst in Aldol condensation reaction between benzaldehyde and heptanal is also demonstrated.

2. Experimental procedure

2.1. Materials and microwave synthesis of K-F zeolite nanocrystals

The rice husk ash (RHA) was chosen as a silica source since the rice husk is an agricultural residue abundantly available in rice producing countries. Typically, the silica was extracted from rice husk using the method as reported in Ref. [43]; amorphous RHA with 97.6% SiO2 was successfully prepared.

The nanosized potassium-form Linde Type F (K-F) zeolite was synthesized from a precursor suspension with the following starting composition of 4 SiO2: 1 Al2O3: 16 K2O: 160 H2O. Initially, a clear aluminolate solution was prepared via dissolving KOH (19.217 g, 85%, QREc) and Al( OH)3 (5.791 g, 98%, ACSOR Organic) in distilled water (47.494 g) at 105 °C for 16 h under continuous stirring (400 rpm). A clear silicate solution was also prepared by mixing KOH (39.013 g, 85%, QREc) and the RHA (6.761 g) in distilled water (37.912 g) followed by stirring (400 rpm) at 90 °C for 2 h. Both the aluminolate and silicate solutions were then cooled to room temperature. The aluminate solution was added slowly into the silicate solution under vigorous stirring (700 rpm). During the mixing process, a thick gel precursor suspension was formed. Hence, stirring by hand with the use of a spatula was required at the end of the mixing process to ensure a homogeneous gel precursor was obtained. The precursor gel mixture was continuously stirred for an additional 10 min. The hydrogel was then transferred into 5 PTFE reaction vessels (30.0 g each) before they were subjected to microwave radiation at 100 °C for different irradiation time intervals (0, 0.5, 0.75, 2 and 10 min) by using an Anton Paar’s microwave reaction system (Multiwave 3000, 900 W output power). The solid products were washed with distilled water repeatedly via high-speed centrifugation (10000 rpm, 20 min) until pH 7 before subjected to freeze drying.

2.2. Characterization of solids

The crystallinity and purity of the solids were studied by X-ray powder diffraction technique (Bruker D8 ADVANCE X-ray diffractometer, Cu-Kα radiation source, λ = 1.5418 Å, step size of 0.01°, scan speed of 0.2°/min). The degree of crystallinity was calculated using the intensity of the three most intense Bragg diffraction peaks at 2θ of 12.68° [110], 29.04° [112] and 30.05° [301], in relation to a reference sample (K-F synthesized at 100 °C for 10 min). The average primary crystallite size of the synthesized zeolite products was estimated by Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$  (1)

where τ is the mean size of the crystalline particles in nm determined at the [110] XRD peak; K is the Scherrer constant related to actual shape of the crystalline, taken as 0.94 (assumes cubical crystallites); λ is the X-ray wavelength (1.5418 Å); β is the full width at half maximum intensity (FWHM), after subtracting the line broadening in radians and θ is the Bragg’s angle. The crystallite size,
crystallographic and morphological features of amorphous particles and zeolite nanocrystals were examined by using a FEI LaB6 Tecnai G² F20 transmission electron microscope (TEM) and a Zeiss Auriga Crossbeam field-emission scanning electron microscope (FESEM) operating at an acceleration voltage of 200 kV and 30 kV, respectively. For SAED pattern, it was obtained in microprobe mode where only the thinnest edges of the crystals were selected for SAED analysis in order to minimize the dynamic effect. The Si/Al ratio of the solids was evaluated by using a XGT-5200 XRF instrument. The infrared (IR) spectra of the samples were recorded with a Bruker Tensor 27 spectrometer using the KBr pellet technique (KBr: sample weight ratio = 200:1). The porosity of crystalline K-F zeolite sample was determined using a Micromeritics ASAP 2010 instrument. The powders (ca. 150 mg) were first degassed at 300 °C under vacuum overnight prior to sorption analysis at −196 °C.

2.3. Catalytic experiments

The catalytic Aldol condensation of heptanal and benzaldehyde was conducted using an Anton Paar’s microwave reaction system (Multiwave 3000) under solvent-free condition. Activated K-F zeolite (1500 g, 300 °C, 2 h), heptanal (7.9 mmol, 97%, Merck) and benzaldehyde (39.6 mmol, 99%, Merck) were loaded into a PTFE autoclave. The autoclave was capped and irradiated (600 W output power) at 180 °C for 50 min. The reaction mixture was withdrawn and analyzed using a gas chromatography (Agilent 7890A) equipped with a DB-5 capillary column. For comparison study, the reaction was also carried out in an oil bath (180 °C) for 33 h.

3. Results and discussion

3.1. Microscopy and spectroscopy study of crystal growth of K-F nanozelite

The crystal growth of nanocrystalline K-F zeolite was followed by powder XRD analysis. The XRD patterns and the plot of degree of crystallinity as a function of time of microwave exposure for the solid products are shown in Figs. 1 and 2, respectively. The initial sample before microwave radiation (0 min) is completely amorphous as only one broad band is observed in the range 2θ = 25°–35° (Figs. 1a and 2) [31]. The morphology of this sample is shown in Figs. 3a and 3b. As can be seen, TEM micrograph is unable to detect the presence of crystalline phase. Instead, it reveals the presence of very small amorphous domains with the size of ca. 8 nm.

As the crystallization time was extended to 0.5 min, the thick gel became less viscous when the sample was taken out. Several XRD diffraction peaks emerge at 2θ = 12.74°, 29.01°, 30.17° and 31.81°, which correspond to the [110], [221], [112] and [301] planes of the K-F crystalline phase, respectively (Fig. 1b). The Bragg diffraction peaks for the samples are significantly broadened, thus revealing the small size of crystalline zeolite domains [52] (10.5 nm as calculated from the Scherrer equation). At this stage, the degree of crystallinity is calculated to be 11.3% (Fig. 2).

The TEM microscopy also reveals significant change in the morphology of sample. As shown in Fig. 3c and d, the initial small amorphous particles with irregular shape have transformed to coral-like feature and the amorphous particle size has increased to ca. 18 nm as a result of the polymerization of the inorganic oligomers. Hence, this indicates that structure re-arrangement of the amorphous solid has taken place. Furthermore, spherical secondary particles (ca. 280 nm) consisted of small primary K-F zeolite nanocrystals (ca. 19 nm) are also observed in the TEM images. As seen, the semi-crystalline crystals are not well formed yet since the crystals with typical shape are unable to be identified.

A sudden increase in the degree of crystallinity from 11.3% to 83.9% was detected after 0.75 min of microwave heating (Fig. 2). As can be seen, all the XRD peaks correspond to EDI crystalline phase are shown (Fig. 1c). The primary crystallite size is 24.8 nm as estimated from the Scherrer equation. With the crystallization time prolonged to 2 min, a further increase in the degree of crystallinity to 90.7% was observed (Fig. 2). At this stage, nanocrystalline zeolite K-F prepared from RHA has a size of ca. 39 nm and exhibits flattened cuboid shape which is different from the EDI-type zeolites reported in the previous study (Fig. 3f) [45]. This novel morphology is important in the preparation of zeolite-based sensors, thin films/membranes, catalysts and nanomedicines where the crystals orientation, shape, size and diffusion path length are mattered [53–55]. In addition, these primary nanocrystals tend to agglomerate to form larger cubic secondary particles (ca. 285 nm) as indicated by TEM images (Fig. 3e and f). Thus, this reveals that the K-F nanocrystals tend to grow starting from a nucleation point.
centre of a small spherule) in an amorphous entity by which the growth mechanism is completely different from that of EMT [31] and LTJ [17] zeolite nanocrystals synthesized in RHA system.

Fully crystalline K-F zeolite was obtained after 10 min of microwave radiation. No additional crystalline phase can be seen in this sample according to XRD pattern (Fig. 1e). The FESEM images of the crystals at different spots were also recorded (Fig. 4). As can be seen, the primary nanocrystals (ca. 49 nm) are grown to form secondary particles of cubical geometries. A TEM image captured on the surface of a K-F single crystal at very high magnification is

![TEM images of samples after (a, b) 0 min, (c,d) 0.5 min, (e,f) 2 min and (g) 10 min of microwave radiation at 100 °C. (h) SAED pattern of K-F single crystal recorded from the sample after 10 min of microwave radiation.](image-url)
shown (Fig. 3g). Clear lattice fringes with a spacing of 0.3 nm is seen expected for EDI-type zeolite (theoretical pore size is 0.32 nm) [44]. The selected area electron diffraction (SAED) pattern of single K-F zeolite crystal viewed along the [010] zone axis was also recorded (Fig. 3h). The zeolite structure shows highly discrete and well-indexed diffraction spots. Both TEM image and SAED pattern show the nanocrystals to be crystalline in nature.

Evidence for the chemical evolution during crystallization process was also studied by analyses of the solid entities. The solids were isolated from the precursor and washed thoroughly before examining with XRF spectroscopy. Table 1 shows the elemental data and Si/Al ratios of the solid products. Initial solid before microwave synthesis has a Si/Al ratio of 1.89 which is closed to the ratio of silica and alumina contents added into the mother liquor. As the crystallization process was occurring in a period of time from 0.5 to 2 min, more Al species from the precursor solution were consumed and incorporated to the solids leading to a further decrease in the Si/Al ratio. This suggests that mass transformation of monomeric and oligomeric species into amorphous and crystalline materials has occurred as proven by XRD and TEM results. The Si/Al ratio reaches constant from 2 min onwards. The final crystalline zeolite product has a Si/Al ratio of 1.26 where the created negative charge of the extraframework is counter-balanced by the basic K⁺ cations. As shown, the Si/Al ratio of the K-F zeolite nanocrystals synthesized from RHA is higher than that of the micron-sized K-F zeolite (Si/Al ratio = 1.15) [45].

Complimentary IR spectroscopy study on the solid products was conducted to follow the crystallization kinetic process. The IR bands are generally broad and no IR bands resonate at 434, 525, 570, 618 and 664 cm⁻¹ for the initial solid product, confirming the amorphous character of this sample (Fig. 5a). These five characteristic bands start to emerge after 0.75 min of microwave irradiation, indicating that the formation of the framework structure of K-F zeolite has occurred which agrees well with the TEM and XRD measurements (Fig. 5c). Meanwhile, the intensity of a band at 859 cm⁻¹, which is corresponding to the T–OH (T = Si or Al) bonds, decreases and it can be due to the condensation of T–OH bonds to form T–O–T bonds during the phase transformation process of the amorphous matrix [21]. This band, however, disappears after 2 min of reaction. Concurrently, the absorption band at 618 cm⁻¹, which is characteristic of 4=1 secondary building units (SBUs) present in K-F zeolite [44], becomes more profound indicating that more K-F zeolite particles have been crystallized (Fig. 5e).

The N₂ sorption isotherm of the K-F zeolite nanocrystals (10 min) is depicted in Fig. 6. Type I adsorption isotherm is not observed for the K-F zeolite. Instead, it exhibits a Type IV adsorption isotherm with a type H3 hysteresis loop. Such phenomenon can be explained by the inability of nitrogen molecules (σ = 3.64 Å) to probe into the micropores of K-F zeolite (σ = 3.2 Å) [56]. As a result, an external surface area of 69 m²/g and a total pore volume of 0.22 cm³/g are measured. Besides, the micropore surface area and micropore volume are negligible since the BET surface area is almost not measurable due to smaller pore size of K-F zeolite than the nitrogen molecular size. Nevertheless, it has textural mesopores of 2.7, 12.9 and 22.4 nm created from close packing of the nano-crystals. Although nitrogen molecule is unable to probe this zeolite, this nanozeolite can have many potential applications such as in hydrogen (σ = 2.89 Å) or helium (σ = 2.60 Å) separation, film

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product phasec</th>
<th>XRF spectroscopy analysisd</th>
<th>Si/Al ratio</th>
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<tr>
<td></td>
<td></td>
<td>Si (%)</td>
<td>Al (%)</td>
</tr>
<tr>
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<td>18.24</td>
<td>9.31</td>
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<td>15.20</td>
<td>11.65</td>
</tr>
<tr>
<td>10.0</td>
<td>K-F</td>
<td>15.17</td>
<td>11.61</td>
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</table>

° Determined from XRD analysis.
° In mass%.

Fig. 4. FESEM images of nanocrystalline K-F zeolite after 10 min of microwave irradiation at different magnifications.

Fig. 5. FTIR spectra of the EDI-type samples extracted after (a) 0 min, (b) 0.5 min, (c) 0.75 min, (d) 2 min and (e) 10 min of microwave treatment at 100 °C.
deposition for sensing application, holography, hydrogen storage, semiconductors, chromophore occlusion and catalysis. Comprehensive work on nanocrystalline K-F zeolite in this aspect is in progress.

3.2. Catalytic behavior and catalyst reusability of K-F nanozeolite

The catalytic behavior of nanocrystalline K-F zeolites was tested in the Aldol condensation between benzaldehyde and heptanal under microwave radiation. Without adding any catalyst, 8% of conversion was achieved after 50 min of microwave radiation. In the presence of K-F zeolite nanocatalyst, the reaction conversion and jasminaldehyde selectivity are increasing with microwave radiation time (Table 2). High conversion rate of 77.1% with 69.5% selectivity to jasminaldehyde is obtained in 40 min. Thus, this study indicates the K-F zeolite nanocrystals are active in this reaction where the catalytic reactivity can be originated from the extra-framework K\(^{+}\) ions located at the external surface and the textural mesopores of the zeolites. The conversion keeps increasing to 79.8% after 50 min but the jasminaldehyde selectivity drops to 65.8% showing that 40 min is the optimized reaction time for this microwave synthesis. On the other hand, Aldol condensation reaction is also catalyzed by K-F zeolite under oil bath heating but with a much lower conversion (54.1%) and a lower jasminaldehyde selectivity (59.8%) under very long reaction time (33 h). Hence, the study reveals that microwave heating not only shortens the reaction time but also enhances the reaction conversion and the selectivity of jasminaldehyde.

A reusability test for K-F nanocatalyst was performed where the used K-F zeolite solid was washed with diethyl ether and activated prior to use. The results show that the catalyst is recyclable since the catalytic performance of recovered catalyst is preserved after five successive cycles (Fig. 7). Thus, it suggests that K-F nanozeolite synthesized from RHA can be used as a potential solid base catalyst besides its potential molecular sieving and other applications.

4. Conclusion

An intensive study of the growth of nanocrystalline K-F zeolite from amorphous RHA assisted with microwave radiation has been carried out at 100 °C in an organo-template-free system. The spectroscopy and microscopy revealed that the crystallization rate of K-F zeolite was significantly enhanced using microwave radiation and K-F zeolite started to nucleate within 0.5 min. The study also revealed that fully crystalline K-F nanocrystals were obtained after 10 min. The nanosized K-F zeolite exhibited good catalytic behavior in Aldol condensation reaction of benzaldehyde and heptanal, and the zeolite is recyclable even after fifth cycle of reaction. From an environmental viewpoint, this work is extremely benign as this strategy can be used to prepare other purely siliceous and aluminosilicate porous materials such as aerogel, zeolites and mesoporous materials in an environmentally friendly way. Undoubtedly, the K-F nanozeolite can also be applied as a potential solid base catalyst apart from its potential molecular sieving, adsorption and ion-exchange applications.

Table 2

<table>
<thead>
<tr>
<th>Microwave condition</th>
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<tr>
<td>Time (min)</td>
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</table>

* Reaction conditions: Benzaldehyde — 39.6 mmol, heptanal — 7.9 mmol, catalyst amount — 1.500 g, reaction temperature — 180 °C, solvent free.

* Conversion of heptanal.
Acknowledgments

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