

Nanocrystalline K-F Zeolite from Rice Husk Silica as an Eco-friendly Solid Base Catalyst for the Synthesis of Jasminaldehyde under Microwave Irradiation

(Nanohablur K-F Zeolit daripada Silika Sekam Padi sebagai Mangkin Bes Pepejal Mesra Alam untuk Sintesis Jasminaldehid di bawah Sinaran Gelombang Mikro)

SIEW-FANG WONG, KRITTANUN DEEKAMWONG, JATUPORN WITTAKAYUN, TAU CHUAN LING, OKI MUZARA, HOOI LING LEE, FAROOK ADAM & ENG-POH NG*

ABSTRACT

Nanocrystalline aluminosilicate F-type zeolite (K-F, EDI-type structure) was synthesized in an organic template-free system using rice husk ash (RHA) silica source and microwave energy. The morphology, crystallite size, chemical composition, crystallographic and basicity properties of the nanocrystals were studied by using various characterization techniques. The results showed that fully crystalline K-F zeolite (Si/Al ratio = 1.26) with flattened cuboid-like shaped could be obtained within 2 min of crystallization which was considerably very fast. In addition, K-F zeolite nanocrystals was also tested as a solid base catalyst in the microwave-enhanced Aldol condensation reaction of heptanal with benzaldehyde and the six catalytic parameters were studied and optimized. The nanosized K-F zeolite crystals showed good catalytic performance in the studied reaction with 77.1% heptanal conversion and 69.5% jasminaldehyde selectivity under optimum reaction condition. The nanocatalyst was reusable and no significant loss in its catalytic reactivity was observed even after five consecutive reaction cycles.

Keywords: Aldol condensation; K-F; nanozeolite; microwave synthesis; organotemplate free

ABSTRAK

Nanohablur aluminosilikat jenis F zeolite (K-F, jenis struktur EDI) telah disintesis dalam sistem bebas templat organik menggunakan sumber silika sekam padi (RHA) dan tenaga gelombang mikro. Morfologi, saiz hablur, komposisi kimia, sifat hablurgrafi dan sifat dasar nanohablur dikaji dengan menggunakan pelbagai teknik pencirian. Keputusan menunjukkan bahawa zeolit K-F menghablur sepenuhnya (nisbah Si/Al = 1.26) dengan bentuk membentuk kuboid rata diperolehi dalam masa 2 minit penghabluran. Selain itu, nanohablur zeolit K-F juga diuji sebagai pemangkin asas pepejal dalam tindak balas pemeluwapan Aldol yang dipertingkatkan oleh gelombang mikro heptanal dengan benzaldeid dan enam ukuran pemangkin dikaji dan dioptimumkan. Zeolit K-F nanohablur menunjukkan prestasi pemangkin yang baik dalam tindak balas yang dikaji dengan penukaran 77.1% heptanal dan jasminaldehid memilih 69.5% di bawah keadaan tindak balas optimum. Nanopemangkin boleh digunakan semula dan tiada kehilangan ketara dalam tindakbalas pemangkinnya selepas lima kitaran reaksi berturut-turut.

Kata kunci: K-F; kodensasi aldol; sintesis gelombang mikro; templat organo bebas; zeolit hablur

INTRODUCTION

Zeolites are hydrated porous aluminosilicate crystalline solids with open three-dimensional framework structures which are built up of tetrahedral AlO_4 and SiO_4 units. Zeolites are commonly used in the applications such as catalysis, separation, adsorption and ion-exchange due to their unique intracrystalline porous structures that are comparable to the molecular dimensions (particularly between 2 and 10 Å) (Bein & Mintova 2005). Recently, nanosized zeolite crystals are widely employed in advanced applications such as in optical layers (Tosheva et al. 2008), drug delivery (Shan et al. 2006), chemical sensors (Ng et al. 2014), biomedical (Rahimi et al. 2015), semiconductors (Bouizi et al. 2005) and others (Majano et al. 2011; Ng et al. 2015c, 2009).

RHA silica has been recently used to synthesize several types of zeolite such as NaA (Azizi & Yousefpour 2010), faujasite-X (Dalai et al. 1985), beta (Prasetyoko et al. 2006), ZSM-5 (Kordatos et al. 2008), LTL (Wong et al. 2012), ZSM-11 (Dey et al. 2012), ZSM-48 (Wang et al. 1998), KF (Wong et al. 2017a, 2017b) and SUZ-4 (Jaronvechatam et al. 2013) zeolites because it is cheap, plentiful and easy to cultivate. Nevertheless, there are only a few articles reporting on the synthesis of zeolite in nanometer scale (<100 nm with at least one dimension) from RHA under conventional heating (e.g. EMT, faujasite-X, KL, and hydroxysilicate) (Ghasemi & Younesi 2012; Ghasemi et al. 2011; Ng et al. 2015a, 2015b; Wong et al. 2012).

Linde Type F zeolite, also known as K-F zeolite is a synthetic EDI-type analogue and its framework structure

composes of interlink chains of T_5O_{10} tetrahedra ($T = \text{Si}$ or Al) (<http://www.iza-structure.org/databases/>). K-F zeolite is a small pore zeolite characterized by its tridimensional pores with two different types of interconnected 8 member ring (8MR) channel systems (diameter of $2.8 \times 3.8 \text{ \AA}^2$ and $2.0 \times 3.1 \text{ \AA}^2$) (<http://www.iza-structure.org/databases/>). K-F zeolite has many applications such as in gas separation and purification (Sherman 1991), waste-water cleaning (Novembre et al. 2014) and soil amendment (Jaccula et al. 2006) because of its high affinity towards ammonium cation (NH_4^+) and unique three dimensional pore system. The synthesis of pure EDI-type zeolite nanocrystals (<100 nm) particularly free of organic template, however, has not yet successful due to the difficulty to find accurate synthesis formulation for synthesizing this nanocrystalline material. Therefore, an attention on this aspect is of the utmost vital and is worth to be further explored.

In this study, we report a rapid and facile microwave synthesis of K-F zeolite nanocrystals using RHA as an alternative silica source. The synthesized zeolite crystals are grown in a $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ hydrogel system free of organic template. The K-F zeolite nanocrystals are then characterized and used as a solid base catalyst in Aldol condensation reaction of heptanal with benzaldehyde.

EXPERIMENTAL SECTION

PREPARATION OF RHA

Rice husk ash (RHA) was chosen as an alternative silica source because rice husk is an agricultural waste abundantly available in rice producing countries. Typically, rice husk (RH), which was collected from a rice mill, was washed with tap water prior to air dried overnight. The dried rice husk was then soaked in 1.5 M HNO_3 solution and shaken for 15 h at 90 rpm to remove inorganic impurities. The acidified rice husk was washed with distilled water until a pH of 7.0 was reached. Next, the rice husk was dried at 100°C overnight and burnt in a muffle furnace at 600°C for 12 h. White amorphous silica ash (RHA) with 97.6% SiO_2 as the final product was obtained.

MICROWAVE SYNTHESIS OF NANOSIZED K-F ZEOLITE

The potassium-form Linde type F (K-F) nanozeolite was synthesized from an organo-template-free precursor with the starting composition of 4 SiO_2 : 1 Al_2O_3 : 16 K_2O : 160 H_2O . At first, potassium hydroxide pellets (19.217 g, 85%, QR&C) and aluminum hydroxide (5.791 g, 98%, ACR&S Organic) were stirred (400 rpm) in distilled water (47.494 g) at 105°C for 16 h to obtain a transparent aluminate solution. In another polypropylene bottle, KOH pellets (39.013 g, 85%, QR&C), RHA (6.761 g) and distilled water (37.912 g) were mixed and stirred (400 rpm) at 90°C for 2 h. The first solution was added dropwise into the silicate solution under vigorous stirring (700 rpm). Hand stirring with a spatula was needed when a thicker gel precursor mixture was formed during the mixing process. The final mixture was continuously stirred for

another 10 min before transferring into PTFE reaction vessels (30.0 g each). The samples were then irradiated with microwave for 2 min (100°C) by using an Anton Paar's Multiwave 3000 microwave reactor (900 W). Next, the solid products were isolated from the mother liquors via high-speed centrifugation (10000 rpm, 20 min). The solid products were washed repeatedly with distilled water until a pH of 7 was reached. The purified K-F zeolite suspensions were then freeze-dried prior to various characterization analyses.

CHARACTERIZATION OF K-F NANOZEOLITE

The purity of the crystalline solid was investigated by a Bruker D8 ADVANCE X-ray diffractometer (Cu-K_α source, $\lambda = 1.5418 \text{ \AA}$). The size, morphology and crystallographic properties of zeolite nanocrystals were determined by using a Zeiss AURIGA Crossbeam field emission scanning electron microscope (FESEM) and a FEI LaB₆ TECNAI G² F20 transmission electron microscope (TEM) operating at 30 and 200 kV, respectively. The Si/Al ratio of the solid products was determined by using a XGT-5200 XRF spectrometer. FT-IR spectrum of fully crystalline K-F nanozeolite was obtained using a Bruker Tensor 27 spectrometer in the wavelength range of $400\text{-}4000 \text{ cm}^{-1}$ (32 scans, 4 cm^{-1} resolution). The BET or external surface area of K-F zeolite nanocrystals was determined using a Micromeritics ASAP 2010 instrument. The solid (ca. 150 mg) was first degassed under vacuum at 300°C for 15 h before the sorption analysis started at -196°C . Temperature-programmed desorption of carbon dioxide ($\text{CO}_2\text{-TPD}$) experiment was performed on a BELCAT-B instrument which was connected to a thermal conductivity detector. The powder sample (ca. 50 mg) was first degassed at 300°C , adsorbed with CO_2 and followed by desorption analysis in the temperature range of 50 to 750°C at a heating rate of $10^\circ\text{C}/\text{min}$.

CATALYTIC STUDY

The Aldol condensation reaction of heptanal and benzaldehyde was carried out in an Anton Paar's Multiwave 3000 microwave reactor. In a typical reaction procedure, K-F nanozeolite (1.500 g), heptanal (7.9 mmol, 97%, Merck) and benzaldehyde (39.6 mmol, 99%, Merck) were added into a PTFE autoclave. The autoclave was tightly capped and irradiated with microwave (600 W) at 180°C for 40 min. The reaction mixture was withdrawn and analyzed using a gas chromatograph (Agilent 7890A) equipped with a DB-5 capillary column. *n*-Decane was used as an internal standard. The identity of the reaction product was confirmed by a GC-MS (Agilent 7000 Series Triple Quad GC/MS) equipped with a HP-5MS (5%-Phenyl)-methylsiloxane capillary column. The reaction was also performed in an oil bath (180°C , 33 h) for comparison study.

The reusability study of zeolite catalyst was conducted as follows: K-F zeolite solid was separated after the first catalytic reaction run. The zeolite solid was washed with diethyl ether (10 mL, 3 times) and dehydrated before being used for the subsequent cycles of catalytic reaction. The reaction mixture was separated again after the reaction and

analyzed using GC. The catalyst after reuse was subjected to XRD analysis.

RESULTS AND DISCUSSION

SYNTHESIS OF K-F ZEOLITE NANOCRYSTALS

Nanosized K-F zeolite was synthesized from RHA free of organic template under microwave radiation. The XRD patterns of the solids before and after microwave heating for 2 min were shown (Figure 1). The data revealed that the solid product before microwave exposure was fully amorphous since only one broad peak was detected in the range $2\theta = 25^\circ$ – 35° (Figure 1(a)) (Ng et al. 2015b). As this precursor was irradiated with microwave for 2 min, all the XRD diffraction peaks resembled to EDI characteristics appeared at $2\theta = 12.74^\circ$, 13.57° , 25.68° , 29.01° , 30.17° , 31.81° and 40.11° , indicating the formation of the K-F crystalline phase (Figure 1(b)). The Bragg diffraction peaks were indexed and assigned to K-F zeolite of tetragonal structure. As seen, the peaks were broad, indicating that small zeolite crystals had been obtained (Ng et al. 2014).

Two FESEM micrographs of K-F zeolite nanocrystals obtained under different magnifications were given in Figure 2(a), 2(b). As shown, the primary nanocrystals were tend to agglomerate and form secondary particles with cubical geometrics. The microscopic study revealed

that the K-F zeolite nanocrystals had a crystallite size of ca. 60 nm (Figure 2(b)). The TEM images of the K-F nanozeolite were also captured (Figure 2(c), 2(d)). The K-F zeolite nanocrystals were in flattened cuboid shape which were different from the EDI-type zeolites reported in the previous study that exhibited prismatic shape (Novembre et al. 2014).

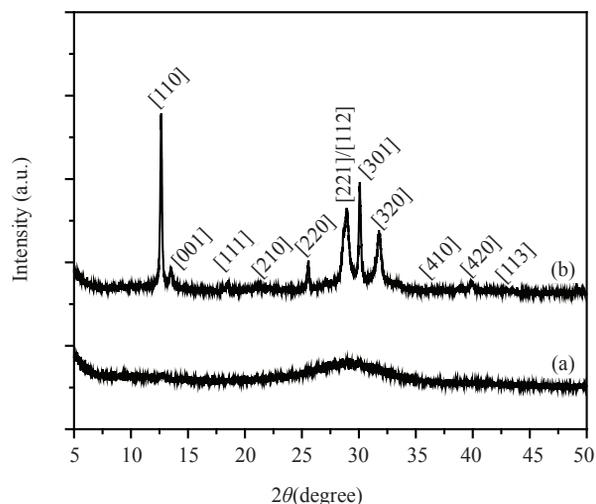


FIGURE 1. XRD diffractograms of solid samples (a) before and (b) after 2 min of microwave irradiation

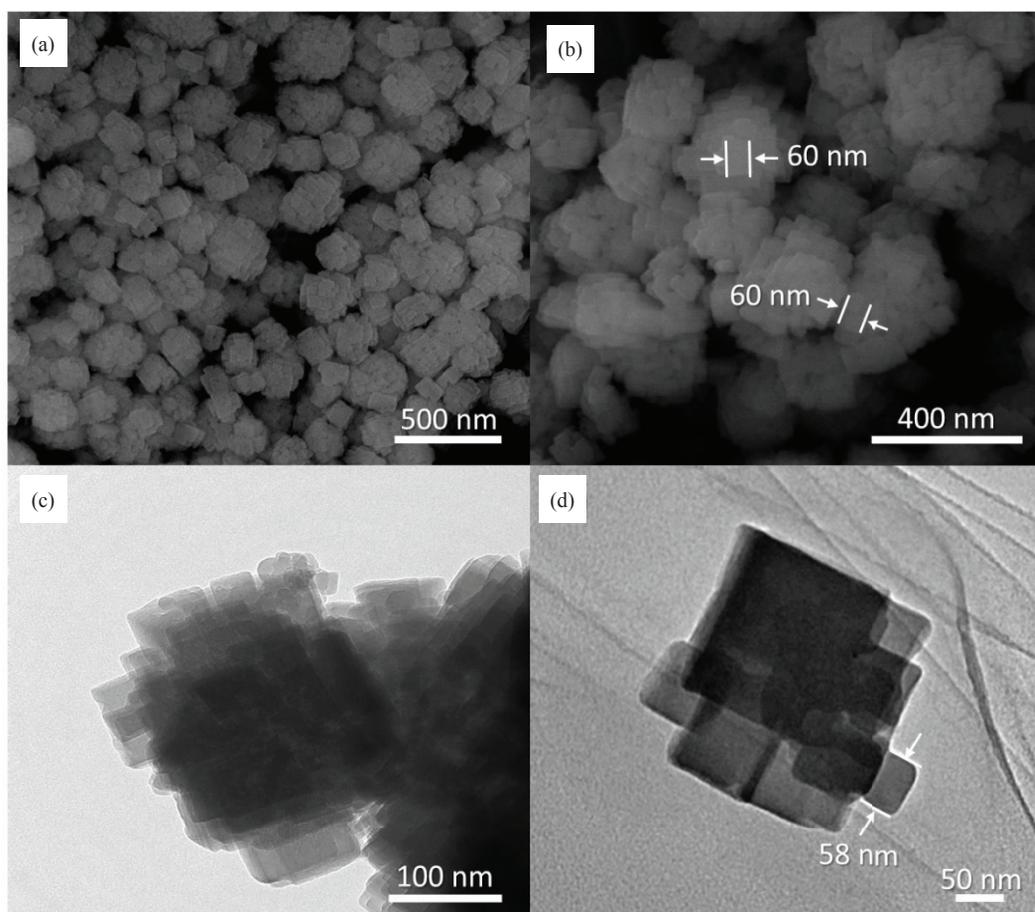


FIGURE 2. (a,b) FESEM and (c,d) TEM images of nanocrystalline K-F

The initial solid product before microwave radiation had a Si/Al ratio of 1.89, which was very near to the ratio of silica and alumina contents of the initial reactant mixture. The Si/Al ratio of the K-F nanocrystals reduced to 1.26 after 2 min of microwave radiation. An increase of Al content in solid could be explained by more Al species from the hydrogel precursor were participating in the construction of K-F zeolite framework structure. This result also indicated that the K-F zeolite nanocrystals possessed surface negative charge by which it was charge-compensated by the extraframework K^+ base cations.

The FTIR spectrum of nanocrystalline K-F was depicted in Figure 3. The IR bands at 3416 and 1648 cm^{-1} were due to the stretching and bending vibration modes of hydroxyl group of adsorbed water molecules (Byrappa & Kumar 2007). The two IR bands at 1020 and 992 cm^{-1} were assigned to the internal vibration of Si–O–T (T = Si, Al) asymmetric stretching modes (Byrappa & Kumar 2007). The absorption band at 847 cm^{-1} could be assigned to the T–OH (T = Si, Al) bonds (Khoo et al. 2013). The vibration band at 664 cm^{-1} was attributed to the symmetric stretching of Si–O–T bond. Moreover, the IR signals at 615 and 578 cm^{-1} were the characteristics of zigzag 8-membered ring subunits present in K-F nanozeolite. The bending vibration of TO_4 (T = Si, Al) was indicated at 434 cm^{-1} (Byrappa & Kumar 2007).

The porosity of K-F nanozeolite was determined by using N_2 sorption analysis. Since the nitrogen molecules ($\sigma = 3.64 \text{ \AA}$) cannot probe into the micropores of K-F zeolite ($2.8 \times 3.8 \text{ \AA}^2$ and $2.0 \times 3.1 \text{ \AA}^2$), therefore the micropore surface area cannot be determined. As a result, only external surface area of 69 m^2/g was measured (Haynes 2014).

The basic properties of nanosized K-F zeolite were evaluated by CO_2 -TPD analysis. Four deconvoluted signals were shown in the CO_2 -TPD profile of K-F nanozeolite (Figure 4). The signal at 257°C was due to the weak basic sites located at the textural pores of the zeolite. The signals centered at 375°C and 470°C were originated from the mild

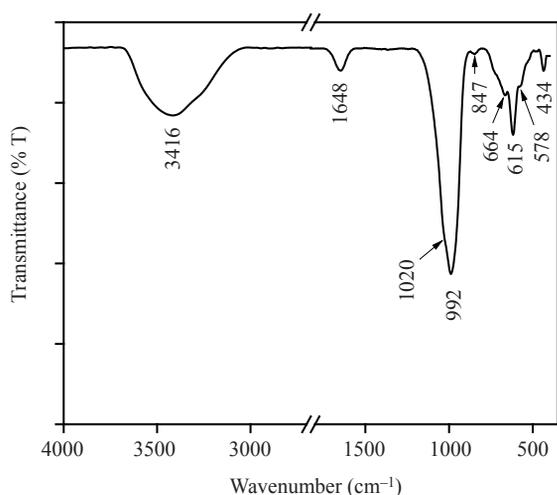


FIGURE 3. FTIR spectrum of the nanosized K-F zeolite synthesized from RHA under microwave radiation

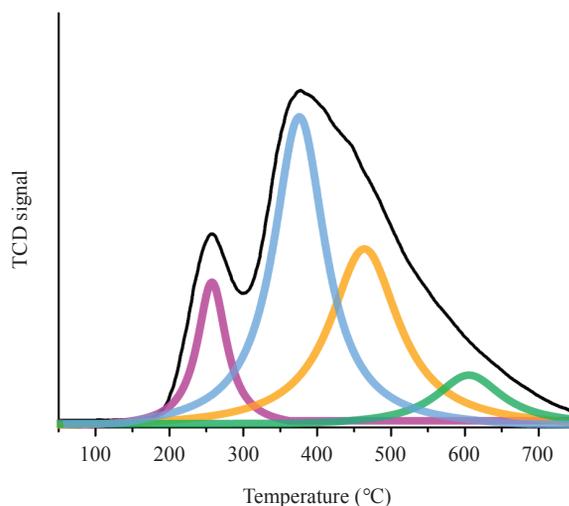


FIGURE 4. CO_2 -TPD profile of K-F zeolite nanocrystals

basic sites located at the external surface of the zeolite. In addition, a weak signal was also detected at 610°C and it was due to the interaction between CO_2 and the strong basic sites located in the micropores of the zeolite. As shown, this band was small due to the difficulty of CO_2 (molecular diameter = 3.3 \AA) to probe this zeolite (pore diameter = 3.2 \AA) (Hardie et al. 2005; <http://www.iza-structure.org/databases/>).

CATALYTIC ACTIVITY STUDIES

Aldol condensation reaction between benzaldehyde and heptanal was chosen as a model reaction to study the potential of K-F zeolite nanocrystals as a solid base catalyst under microwave condition. The effect of reaction parameters, such as the amount of catalyst, reaction temperature, microwave irradiation time, type of solvent, reaction method and heptanal to benzaldehyde molar ratio, on the conversion of heptanal and the selectivity of jasminaldehyde were carefully studied.

EFFECT OF CATALYST AMOUNT

The effects of catalyst amount on the heptanal conversion and the selectivity of jasminaldehyde were studied at 180°C for 40 min by varying the amount of K-F catalyst from 0 to 2.5 g while the heptanal to benzaldehyde molar ratio was kept constant (Figure 5). Noticeably, the conversion of heptanal increased with increasing the catalyst amount. On the other side, the selectivity of jasminaldehyde also increased from 67.4% to 69.5% when the catalyst loading was increased from 0.5 to 1.5 g. On further increasing the catalyst amount to 2.0 and 2.5 g, the selectivity, however, reduced to 60.4% and 63.6%, respectively. This phenomenon can be explained by the fact that when high catalyst amount is used, the catalyst tends to promote self-condensation of heptanal than the condensation of heptanal with benzaldehyde (Hamza & Nagaraju 2015). Hence, further optimization studies were performed by using 1.5 g catalyst.

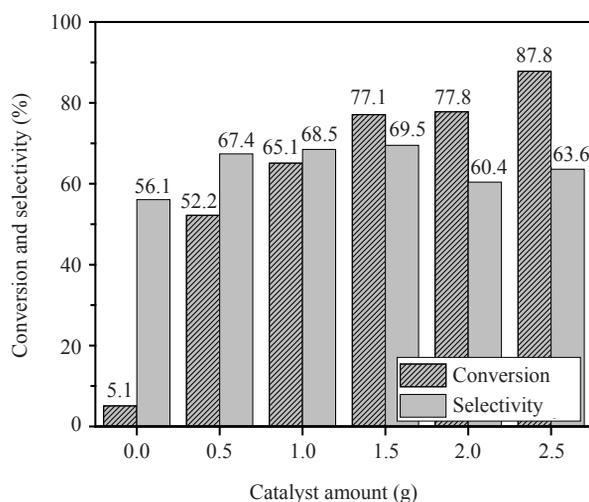


FIGURE 5. Effect of catalyst amount on the conversion of heptanal and selectivity of jasminaldehyde. Heptanal:benzaldehyde molar ratio = 1:5, temperature = 180°C, microwave irradiation time = 40 min

EFFECT OF REACTION TEMPERATURE

The effect of reaction temperature was also investigated in a wide temperature range from 120°C to 200°C. It was observed that increase in conversion of heptanal was accompanied by decrease in selectivity of jasminaldehyde upon increasing reaction temperature (Figure 6). The conversion of heptanal increased from 55.1% to 82.6% by increasing the reaction temperature from 120°C to 200°C. This implies that high temperature can promote the reaction as Aldol condensation is an endothermic reaction (Abbaspurad & Moradi 2011). However, the selectivity of jasminaldehyde at 200°C reduced to 64.9% since high reaction temperature favored the formation of undesirable side product (2-pentyl-non-2-enal). Based on these results, the optimum temperature for this reaction was 180°C.

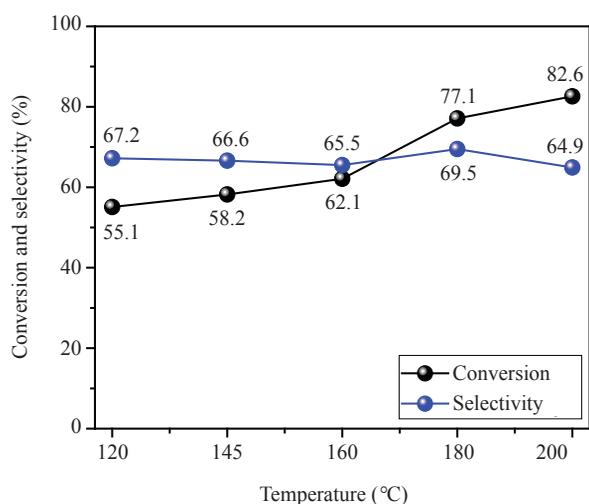


FIGURE 6. Effect of reaction temperature on the conversion of heptanal and the selectivity of jasminaldehyde. Heptanal:benzaldehyde molar ratio = 1:5, 1.5 g K-F catalyst, microwave irradiation time = 40 min

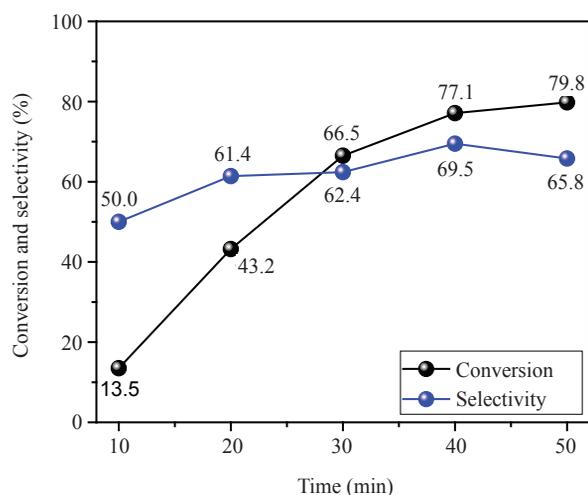


FIGURE 7. Conversion of heptanal and selectivity of jasminaldehyde with respect to reaction time. Heptanal:benzaldehyde molar ratio = 1:5, 1.5 g K-F catalyst, reaction temperature = 180°C

EFFECT OF REACTION TIME

The effect of reaction time on the Aldol condensation of heptanal and benzaldehyde was studied at various times. As seen from Figure 7, the conversion of heptanal increased exponentially with reaction time. For example, 13.5% conversion of heptanal with 50% selectivity to jasminaldehyde was recorded in 10 min reaction time. By increasing the reaction time from 10 to 40 min, the conversion of heptanal increased to 77.1% with 69.5% jasminaldehyde selectivity. Further increase in the reaction time to 50 min caused in 79.8% heptanal conversion but the jasminaldehyde selectivity reduced to 65.8%. Hence, the optimum reaction time was set to 40 min.

EFFECT OF REACTION METHOD

The reaction was also performed in an oil bath (180°C) for 33 h for comparison study (Table 1). Noticeably, both reaction methods gave different catalytic performance. For microwave heating, high conversion rate of 77.1% with 69.5% jasminaldehyde selectivity was achieved within 40 min. In contrast, a much lower conversion (54.1%) with lower jasminaldehyde selectivity (59.8%) was achieved under conventional oil bath heating even after long reaction time (33 h). Therefore, it can be concluded that microwave heating not only reduces the reaction time but also improves the reaction conversion and jasminaldehyde selectivity.

EFFECT OF HEPTANAL TO BENZALDEHYDE MOLAR RATIO

The effect of heptanal to benzaldehyde molar ratio was investigated by using various molar ratios in the range of 1:3 to 1:13 (Figure 8). An increase in the selectivity of jasminaldehyde was observed with increasing the molar ratio of benzaldehyde-heptanal. For example, 66.1% heptanal conversion with 56.7% jasminaldehyde selectivity was found at heptanal to benzaldehyde molar ratio of

TABLE 1. Conversion of heptanal and selectivity of jasminaldehyde with K-F nanocatalyst under microwave and oil bath heatings^a

Microwave heating			Oil bath heating		
Time (min)	Conversion (%) ^b	Jasminaldehyde selectivity (%)	Time (h)	Conversion (%) ^b	Jasminaldehyde selectivity (%)
10	13.5	50.0	6	8.4	21.9
20	43.2	61.4	13	27.0	32.5
30	66.5	62.4	17	41.6	46.7
40	77.1	69.5	24	50.8	54.1
50	79.8	65.8	33	54.1	59.8

^aReaction conditions: Benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst amount = 1.5 g, reaction temperature = 180°C, ^bConversion of heptanal

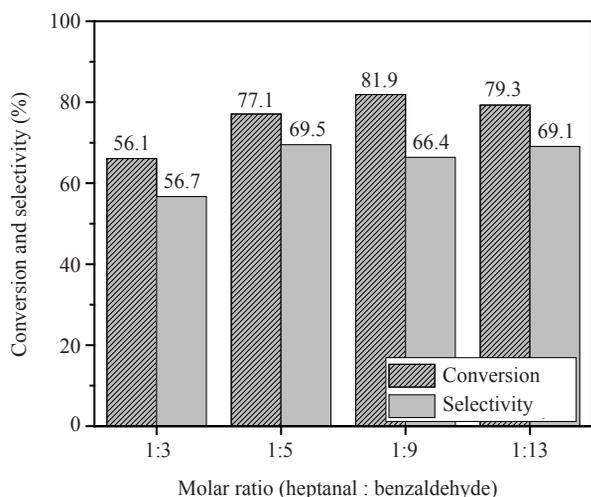


FIGURE 8. Effect of heptanal to benzaldehyde molar ratio on the conversion of heptanal and selectivity of jasminaldehyde. 1.5 g K-F catalyst, reaction temperature = 180°C, microwave irradiation time = 40 min

1:3 and it increased to 81.9% conversion with 66.4% jasminaldehyde selectivity upon increasing the heptanal to benzaldehyde molar ratio to 1:9. However, the heptanal conversion reduced to 79.3% with further increasing the molar ratio to 1:13 while the jasminaldehyde selectivity slightly increased to 69.1%. This is due to the fact that higher benzaldehyde concentration in the reaction solution can lead to competitive adsorption between benzaldehyde and heptanal on the surface of catalyst and thus reducing the heptanal conversion. In addition, the self-condensation

product of heptanal (2-pentyl-non-2-enal) decreased upon increasing the heptanal to benzaldehyde molar ratio. This indicated that at higher benzaldehyde concentration, the condensation rate of heptanal with benzaldehyde was much faster, thus significantly suppressed the self-condensation of heptanal.

EFFECT OF SOLVENT

The synthesis of jasminaldehyde was also performed in the presence and absence of solvent (Table 2). Five types of solvents with different polarity (in E_T^N scale) (Ng et al. 2011; Zou et al. 2001), namely dichloromethane, acetonitrile, DMSO, ethanol and water, were studied. From the data obtained, it was evidenced that the catalytic reactions performed in polar solvents exhibited better conversion while the selectivity of jasminaldehyde was independent of the solvent polarity. On the other hand, the solvent-free system showed more superior catalytic performance compared to the solvent-containing catalytic systems. The results imply that solvent media can hamper the conversion of the reactants due to the dilution of the reactants concentration.

CATALYST COMPARISON STUDY

The catalytic performance of K-F nanozeolite for the synthesis of jasminaldehyde was also compared with the other zeolitic catalysts (Table 3). The present study indicated that microwave-enhanced Aldol condensation reaction using K-F nanozeolite catalyst exhibited much higher conversion (75.6%) with better selectivity towards

TABLE 2. Effect of solvent on conversion of heptanal and selectivity of jasminaldehyde^a

Solvent	E_T^N scale	Conversion ^b (%)	Selectivity (%)	
			Jasminaldehyde	2-Pentyl-non-2-enal
Dichloromethane	0.309	14.0	63.6	36.4
DMSO	0.444	23.8	84.1	15.9
Acetonitrile	0.460	47.2	79.2	20.8
Ethanol	0.654	52.7	71.6	28.4
Distilled water	1.000	56.9	72.7	27.3
Solvent-free	-	77.1	69.5	30.5

^aReaction conditions: Benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst amount = 1.500 g, reaction temperature = 180°C, reaction time = 40 min; solvent volume = 4 mL. ^bConversion of heptanal

TABLE 3. Comparison of K-F nanocatalyst with closely related catalyst systems under reflux condition

Catalyst	Heptanal conversion (%)	Jasminaldehyde selectivity (%)	References
K-F nanozeolite	75.6	67.2	This work
H-Y	53.0	52.0	Climent et al. 2001
Cs-HY	25.0	49.0	Vrbkova et al. 2016
H-AlMCM-41	75.0	29.0	Sharma et al. 2008
H-Beta	93.0	21.0	Climent et al. 2001
NaY	24.0	36.0	Vrbkova et al. 2016
Cs-NaY	46.0	24.0	Vrbkova et al. 2016

jasminaldehyde (67.2%) than those using other base catalysts (Cs-HY, H-AlMCM-41, NaY, Cs-NaY). On the other hand, the catalytic systems using H-AlMCM-41 and H-Beta catalysts showed higher heptanal conversion (>75%) but they were not selective to jasminaldehyde (<29%) due to the use of acidic and large pore catalysts that lead to the preferential formation of unwanted self-condensation product (Climent et al. 2001).

CATALYST REUSABILITY TEST

Catalyst reusability is a major problem for solid catalysts in liquid phase reaction. Hence, a reusability test for K-F nanozeolite was performed. The results indicated that the catalyst was recyclable as the reactivity of the recovered zeolite nanocrystals was preserved after five successive cycles (conversion ca. 75.6% and selectivity to jasminaldehyde = 67.2%) (Figure 9). The slight decrease in the catalytic activity after each cycle might be due to the physical loss of the catalyst during separation. Apart from handling loss, the decrease in catalytic activity may be due to the adsorption of products or substrates on the surface of catalyst. On the basis of these results, it was suggested that the extraframework K⁺ cations were strongly bounded to the zeolite external surface *via electrostatic attraction* force (Arbuznikov et al. 1998) and thus it remained catalytically

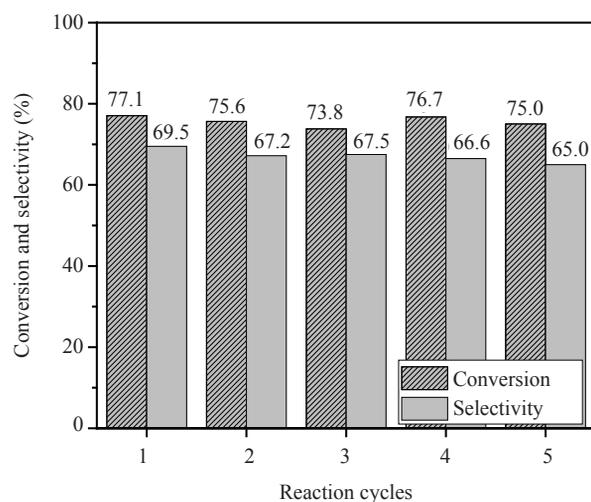


FIGURE 9. Product conversion and selectivity of jasminaldehyde from recyclability test of K-F zeolite nanocatalyst in Aldol condensation reaction

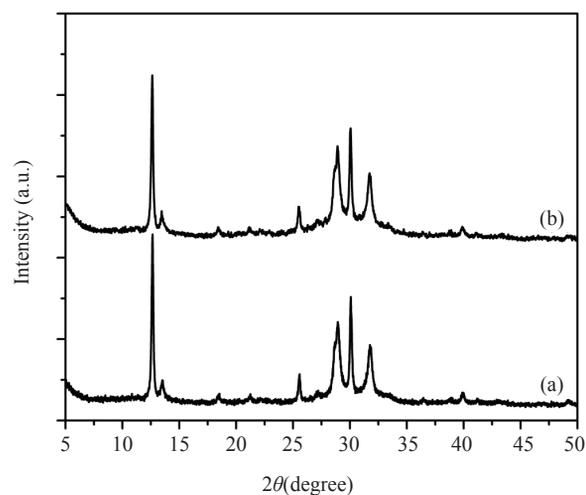


FIGURE 10. XRD diffractograms of (a) fresh K-F nanocatalyst and (b) reused K-F catalyst after fifth cycle of catalytic reaction

active to the Aldol condensation even after several reaction runs. The XRD patterns of fresh and reused K-F catalysts were also recorded (Figure 10). It was shown that no significant loss in crystallinity was observed indicating that the framework structure remained intact after fifth cycle of catalytic reaction. Thus, the catalytic study showed that K-F nanozeolite synthesized from RHA silica can be used as a potential solid catalyst besides its potential molecular sieving, ion-exchange and adsorption applications.

CONCLUSION

In conclusion, nanocrystalline K-F zeolite had been successfully synthesized from RHA using microwave-assisted hydrothermal technique. The results indicated that fully crystalline K-F nanocrystals could be obtained within very short synthesis time (2 min) without utilizing any harmful and expensive organic templates. The resulting primary zeolite nanoparticles (Si/Al ratio = 1.26) had a size of 60 nm and exhibited flattened cuboid shape and they tended to form larger secondary particles with cubical geometries. CO₂-TPD analysis showed that nanocrystalline zeolite K-F possessed 4 types of basic sites with different strength. The catalytic activity of K-F zeolite nanocrystals was tested in the Aldol condensation reaction of heptanal with benzaldehyde under microwave

condition and the effects of catalytic parameters had also been studied and optimized. The nanocatalyst was reusable and its catalytic reactivity was preserved even after five consecutive reaction cycles. From an environment viewpoint, this work is extremely benign as this zeolite is prepared in an environmentally friendly way by using (1) rapid and energy saving microwave synthesis approach, (2) renewable agricultural biomass, and (3) organo-template free system.

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- Siew-Fang Wong, Hooi Ling Lee, Farook Adam & Eng-Poh Ng*
School of Chemical Sciences
Universiti Sains Malaysia
11800 USM, Pulau Pinang
Malaysia
- Krittanan Deekamwong & Jatuporn Wittayakun
School of Chemistry, Institute of Science
Suranaree University of Technology
Nakhon Ratchasima, 30000
Thailand
- Tau Chuan Ling
Institute of Biological Sciences
Faculty of Science
University of Malaya
50603 Kuala Lumpur, Federal Territory
Malaysia
- Oki Muraza
Center of Research Excellence in Nanotechnology and
Chemical Engineering Department
King Fahd University of Petroleum & Minerals
Dhahran 31261
Saudi Arabia

*Corresponding author; email: epng@usm.my

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