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The effect of structural properties of natural silica precursors in the mesoporogen-free synthesis of hierarchical ZSM-5 below 100 °C

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The low-temperature synthesis of zeolite ZSM-5 below 100 °C is gaining new attention. This is due to the fact that such synthesis may simultaneously implement the introduction of mesopores into crystalline microporous zeolite structure. Herein, we report the use of natural silica precursors from rice husks in the mesoporogen-free synthesis of hierarchical ZSM-5 below 100 °C and their structural properties which govern the course of crystallization. Rice husks are agricultural wastes with high silica content, which should be exploited to give a positive impact, i.e. highly value-added materials. In this study, the amorphous silica from rice husks was extracted using sequential base-acid treatment. The extracted silica was similarly reactive as Ludox HS-40, even with the reduced amounts of the organic structure-directing agent (OSDA). The product was highly crystalline ZSM-5 with spherical morphology composed of small crystallites, enabling the presence of intercrystallite mesopores. The subjection of extracted silica into the calcination at 550 °C for 6 h, prior to the low-temperature synthesis, altered the silica structure via hydroxyl condensation. The distinct structural properties affected the occurring crystallization in which the resulted products were ZSM-5–disordered-mesoporous silica composites. The possible mechanisms of these two different results may involve the dual roles of tetrtrapropylammonium ion (TPA⁺) as zeolite OSDA and non-templating structure directing agent. These insights were based on the spectroscopic (FTIR, Raman, ²⁹Si and ⁷⁷Al MAS NMR spectroscopy), microscopic (TEM and HRTEM) and physicochemical characterizations (XRD and N₂ adsorption-desorption isotherm).

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1. Introduction

Rice husks are the major by-product of rice production with annual global production of 120 million tons, thus, established as the second highest-volume agricultural processed residues, after sugarcane bagasse [1]. Rice husks are recognized as the abundant source of natural silica with the mass content around 15–28 wt% depending on several factors, such as climate, rice variety, and geographical condition [2]. This means that there are around 18 million tons of silica from rice husk produced each year across the globe. With this huge amount, the development of products with high-added value is desired. However, rice husk is commonly disposed as waste through open-field burning [3,4]. Exploration for making the full use of rice husk have been investigated for decades. However, the applications of rice husk have been currently focussing on those of low-added value, such as fertilizer additives and paving materials [5].

To address this issue, rice husks must be considered as the sustainable silica source for the fabrication of silicon-based materials with high-added value [6]. Before being utilized as silica precursor, rice husk is commonly burned at high temperature to form rice husk ash (RHA) with various silica content (80–98%) depending on several parameters, such as burning conditions, rice variety, the climate and the geographic area [2,7]. However, this process usually leads to the formation of crystallized phases, which are relatively inactive in the preparation of silicon-based materials and also involves high energy consumption [7–9]. Moreover, the lignocellulosic content of rice husks will be fully damaged during calcination whereas these are important sustainable materials for energy and chemicals production [10,11]. Therefore, alternative
route for extracting the silica content from rice husk was applied, i.e. sequential base-acid treatment, to avoid the occurring crystallization, high energy consumption, and the loss of lignocellulosic content.

Among silicon-based materials with high-added value, zeolites are of huge advantage due to their wide range of applications covering catalyst [12,13], sorbent [14], membrane [15] and drug delivery [16]. Zeolites are a class of microporous (<2 nm) crystalline aluminosilicate materials arranged of T04 tetrahedral (T = tetrahedral Si or Al). Among many types of zeolite, one of them is ZSM-5 (MFI topology), a major catalyst in petroleum and fine chemical industries. Thus, the conversion of low-cost natural silica source to ZSM-5 materials will be very beneficial from the industrial and technological point of view. The synthesis of ZSM-5 is commonly performed via hydrothermal method at high temperature above 100 °C using tetrapropylammonium ion (TPA⁺) as organic-structure-directing agent (OSDA) [17]. Recently, we have reported the low-temperature synthesis of ZSM-5 below 100 °C. The strategy was to utilize a dense gel system with less amount of water in which the reactants are highly concentrated to accelerate the zeolite crystallization below 100 °C [18]. This way, the amount of OSDA can also be drastically reduced. The study opens the possibility of the formation of mesopores due to the low temperature condition and another ability of TPA⁺ called non-templating structure directing, without the addition of mesopore-generating agent (mesoporegen) [18-22]. Moreover, Ding et al. recently reported that Al zonning might be the key to the hierarchically porous ZSM-5 formation in the absence of mesoporegen [23]. The presence of mesoporosity may overcome the classical molecular diffusion issue within the zeolite framework to enhance the overall catalytic performance.

Several efforts have been made to synthesize ZSM-5 using rice husk ash as the silica source. However, as mentioned before, the problem lies in the calcination of rice husks to obtain silica which leads to the formation of crystallized phases, the very less-reactive precursors for the synthesis of zeolite. This problem may be overcome, but, the hydrothermal synthesis at high-temperature is required, generally along with the immense amount of OSDA [4,7,24-27]. To the best of our knowledge, the use of rice husks for the synthesis of zeolites is limited to the use of hydrothermal method. In this contribution, we report the synthesis of ZSM-5 below 100 °C using rice husks as silica precursors. The silica is reactive enough to undergo crystallization toward hierarchically porous ZSM-5. The calcination of silica leads to the alteration of its structural properties, which govern the course of crystallization below 100 °C.

2. Experimental section

2.1. Materials

Rice husk (RH) was obtained from Lombok, West Nusa Tenggara, Indonesia and further treated to be utilized as the silica source. The other reactants were Ludox (HS-40) (colloidal silica, Sigma Aldrich), sodium aluminate (NaAlO₂, Sigma Aldrich), tetrapropylammonium bromide (TPABr, Merck), sodium hydroxide (NaOH, Merck), nitric acid (HNO₃, Merck) and deionized water (H₂O). All commercial reactants were in reagent grade and used directly without further purification.

2.2. Silica extraction from rice husk

The silica from rice husk was extracted using sequential base-acid treatment. The as-received rice husk was washed with water and sun-dried for two consecutive days. The silica extraction from RH was conducted using sequential base-acid treatment. In typical extraction, 22.5 g of RH were added to 250 mL of 1.5 wt% NaOH solution and heated at 100 °C for 12 h. The mixture was subsequently allowed to cool to ambient temperature and then filtered to obtain the brown filtrate. 10 wt% HNO₃ solution was added drop-wise to the filtrate until the pH is below 7, indicated by the formation of brown gels. These gels were subsequently washed with hot deionized water and filtered until the brown color turned to be white. The white gels were dried at 100 °C overnight to obtain the white powder which would be used as silica source in the synthesis of ZSM-5. The as-extracted silica was denoted as RH.

To examine the effect of calcination, RH was subjected to calcination in air at 550 °C for 6 h. The obtained powder was denoted as RHC. Both RH and RHC were used as silica source in this study. As comparison, Ludox was also investigated because it is a typical and commercially available silica source for the synthesis of silica-based materials, including ZSM-5.

2.3. Synthesis of ZSM-5 below 100 °C

The synthesis of ZSM-5 in this study was performed as follows: NaAlO₂, NaOH solution (50 wt%), TPABr, and deionized water were mixed together in a polypropylene bottle and stirred for 15 min. Subsequently, RH was added to the mixture and stirred for another 15 min. The final molar compositions were 1.0 SiO₂: 0.004 Al₂O₃: 0.07 TPABr: 0.12 NaOH: 8, similar to those of our previous report [18]. The TPASi ratio was much lower than that of a previous study by Wang et al. in which the TPASi ratio was 0.24 [20-22]. It should be also noted that additional organic compounds which serve as mesoporegen is also not included in this study. The PP bottle was then heated at 90 °C for 96 h in an oven under static conditions. After the required time, the polypropylene bottle was allowed to cool to ambient temperature. Subsequently, the solid product was filtered, washed, and dried at 100 °C for 4 h. The as-synthesized product was calcined in the air atmosphere at 550 °C for 6 h and denoted as RH-ZSM-5. The crystalline yield of was calculated from the weight of silica incorporated in zeolite phase and silica weight used in the initial mixture.

The synthesis of ZSM-5 using RHC and Ludox was also performed using the same molar compositions and conditions as those of RH-ZSM-5. The product obtained by using RHC and Ludox as silica sources were denoted as RHC-ZSM-5 and Ludox-ZSM-5, respectively.

2.4. Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 Discover diffractometer with a Cu Kα beam (λ = 1.54 Å). The patterns were recorded at 2θ of 3–50° with a step size of 0.02°. Before the measurement, samples were ground and placed in a round and flat specimen holder with a fixed sample thickness of 3 mm. The relative crystallinity of each sample was calculated by integrating area of XRD reflections at 2θ of 22–25° and comparing it with that of ZSM-5 having perfect coffin-type morphology, assuming 100% crystallinity [18]. Scherrer equation was employed to calculate the size of ZSM-5 crystallites.

X-ray fluorescence (XRF) analyses were performed on a PANalytical Axios mAX spectrometer to determine the chemical composition of RH and RHC.

Scanning (SEM), transmission electron microscopy (TEM), high-resolution-TEM (HR-TEM) imaging were performed on JEOL-JSM-6510LV, JEOL-JEM-1400, and JEOL-JEM-2010 microscopes, respectively.

Quantachrome Autosorb iQ-MP instrument was utilized to measure N₂ adsorption-desorption isotherms. The measurement was performed in liquid N₂ medium at 77 K. Prior to its measure-
ment, each sample was degassed at 200 °C for 6 h. The specific surface area ($S_{BET}$) was calculated using Brunauer-Emmett-Teller (BET) method while micro- and mesoporosity were discriminated by using t-plot method. The Non Local Density Functional Theory (NLDFT) method was applied to the adsorption branch of the isotherm assuming the cylindrical pore model to obtain the distribution of the mesopores. The total pore volume ($V_{tot}$) was calculated at the point $P/P_0 = 0.99$.

The FTIR spectra were measured using a Bruker Alpha FTIR spectrometer with a spectral resolution of 4 cm$^{-1}$ at room temperature. Prior to the measurement, samples were prepared as KBr pellets. FTIR spectra were fitted using a Gaussian function.

The Raman spectra were measured on a Bruker Senterra using a 532 nm excitation. All spectra was recorded at room temperature with a spectral resolution of 4 cm$^{-1}$ using 20 mW power output.

Agilent DD2 500 MHz was utilized to measure the $^{29}$Si and $^{27}$Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra at resonance frequencies of 99.31 and 130.28 MHz, respectively. The samples were spun at a rate of 9 kHz with a recycle delay of 5 s and a pulse width of 1.0 μs. $^{29}$Si MAS NMR spectra were reported relative to tetramethylsilane (TMS) using tetrakis(trimethylsilyl)silane (TTMSS) as the external reference while $^{27}$Al MAS NMR spectra were referenced to Al(NO$_3$)$_3$. The NMR spectra were fitted using a Gaussian function.

3. Results and discussion

3.1. Evaluation of silica sources

There were three silica sources being utilized in this study, i.e. RH, RHC and Ludox. RH, for instance, was obtained by applying sequential base-acid treatment to the as-received rice husk. Silica in rice husk was originated from silicic acid (H$_4$SiO$_4$) and its ionic species (H$_3$SiO$_4$), which were absorbed by rice (Oryza sativa) from the soil. Silica was deposited as amorphous phase around the cellulose-based micro-matrices on the cell walls. Previously, it was reported that base treatment could break the cell walls by dissolving hemicellulose and lignin as well as swelling cellulose [28]. Thus, albeit silica was obstructed by the cell walls, the base treatment still could dissolve silica as sodium silicate, according to Eq. (1).

$$2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)$$

Moreover, sodium silicate could be simply converted into silica by the addition of acid solution according to Eq. (2).

$$2\text{HNO}_3 + \text{Na}_2\text{SiO}_3 \rightarrow \text{SiO}_2 + 2\text{NaNO}_3 + \text{H}_2\text{O} \quad (2)$$

As the pH of the solution was below 7, silica gel started to form, showing that silica from rice husks was successfully extracted. From 100 g of the raw rice husks, 24 g of RH could be obtained. As characterized using XRF, the silica content of RH was 70 wt% suggesting that the sequential base-acid treatment was an effective method to extract silica from rice husks. Further calcination of RH at 550 °C for 6 h resulted in RHC with higher silica content, about 82 wt%.

Fig. 1 depicts the XRD patterns of the silica sources. As seen, each pattern showed a broad hump around 2θ of 15–35° without any crystalline peak confirming the amorphous silica phase (Fig. 1a). Furthermore, each pattern was fitted using a pseudo-voigt function to obtain insight on the structural properties by means of the full width at half-maximum (FWHM) values as well as hump positions (Fig. 1b). Ludox exhibited the lowest hump position and the broadest FWHM followed consecutively by RH and RHC. This implied that Ludox had more disordered structure that those of RH and RHC. Moreover, RHC had less-broad FWHM and higher hump position, which indicated the re-arrangement of silica structure via the condensation of hydroxyl bonds during calcination into less-disordered structure [2].

The three silica sources were further analyzed using FTIR spectroscopy, as depicted in Fig. 2. The information about the Si–O covalent bonds were located in the wavenumber around 1400–3400 cm$^{-1}$, while the band at 1650 cm$^{-1}$ corresponded to the adsorbed water molecules bending vibrations [29]. The symmetric stretching vibrations of Si–O–Si bonds arose at 809 cm$^{-1}$ while the intense band at 1095 cm$^{-1}$ and the shoulder at 1215 cm$^{-1}$ were attributed to the transversal optical (TO) and longitudinal optical (LO) modes of the Si–O–Si asymmetric stretching vibrations, respectively [29]. Moreover, the band at 965 cm$^{-1}$ corresponded to the Si–O in-plane stretching vibrations of the Si–OH bonds.

![Fig. 1. (a) XRD patterns and (b) plot of full width at half-maximum versus hump position of each pattern of the silica sources used in this study.](image-url)
We found that the proportion of the band at 965 cm\(^{-1}\) of RHC was lower than that of RH, representing the reduction of the number of silanol groups. In addition, due to calcination, the band at 1095 cm\(^{-1}\) was slightly decreased, but a pronounced increase in the band at 1215 cm\(^{-1}\) was also observed, which indicated that more Si–O–Si bonds were formed. As for Ludox, it possessed the highest proportion of silanol groups with the minimum amount of Si–O–Si bonds. These results indicated the occurring condensation of hydroxyl groups to form more Si–O–Si bonds during the calcination.

Fig. 3 depicts the Raman spectra of Ludox HS-40, RH and RHC. Typically, for silica materials, bands at Raman shift of 220–650 cm\(^{-1}\) and 700–1100 cm\(^{-1}\) were attributed to TO\(_4\) (T = Si or Al) ring bending and T–O stretching vibration modes, respectively \([30,31]\). In detail, the band at 300–400 cm\(^{-1}\) was related to the five-membered rings, 400–450 cm\(^{-1}\) to six-membered rings, 490–560 cm\(^{-1}\) to four-membered rings, and 600–650 cm\(^{-1}\) to three-membered rings \([30,31]\). All three silica samples showed the characteristic spectral features at 440 and 490 cm\(^{-1}\) corresponding to the bending modes of six- and four-membered rings, respectively. The spectra of RH is similar to that of Ludox, except for a small band at 600 cm\(^{-1}\) attributed to the three-membered rings \([30,31]\). Upon the calcination of RH, this band became more pronounced indicating the formation of more three-membered rings. Concomitantly, a new band at 925 cm\(^{-1}\), located in the Raman shift range of T–O stretching mode, was observed in Raman spectra of RHC. This band was not present in the spectra of both Ludox and RH. The distinct spectral features of RHC might be the result of the silica structure re-arrangement of silica structure during calcination, as also suggested by the aforementioned characterizations. The structural differences between these silica samples should influence the crystallization of ZSM-5 below 100 °C in particular.

3.2. Effect of the silica sources in the synthesis below 100 °C

Fig. 4 depicts the XRD patterns of the products synthesized from three silica sources. Ludox-ZSM-5 and RH-ZSM-5 appeared to be highly crystalline, whereas RHC-ZSM-5 was less-crystalline with the significant presence of amorphous phase. The calculated crystallinity of Ludox-ZSM-5, RH-ZSM-5, and RHC-ZSM-5 were 98%, 94% and 40%, respectively. In addition, the crystalline yield of Ludox-ZSM-5, RH-ZSM-5, and RHC-ZSM-5 were 79%, 79% and 35%, respectively. It appeared that the calcination rendered RHC to be less-reactive to undergo the crystallization below 100 °C. Based on Scherrer equation, the crystallite size of Ludox-ZSM-5, RH-ZSM-5 and RHC-ZSM-5 were 72, 55, and 31 nm, respectively. The smallest crystallite size of RHC-ZSM-5 might be because of the incomplete crystal growth since the amorphous phase was still present.
Further analyses were performed using Raman measurements. Fig. 5 depicts Raman spectra of TPABr, as-synthesized and calcined samples of the products. All spectra showed a band at 380 cm\(^{-1}\) which corresponded to the five-membered rings of ZSM-5 structure [30,31]. This band was very sensitive to the presence of ZSM-5 phase, thus, its presence unambiguously showed the formation of ZSM-5 structure [32]. Nevertheless, Raman spectra of RHC-ZSM-5 still exhibited pronounced bands around 440 and 490 cm\(^{-1}\) generated by the six- and four-membered rings, respectively. These bands are the main spectral features of amorphous silica phase. Differently, these bands were not shown by Raman spectra of Ludox-ZSM-5 and RH-ZSM-5 confirming their fully crystallized phase. The bands in the spectral range between 750 and 1500 cm\(^{-1}\) were assigned to H–C–H bending vibration modes of TPA\(^+\) [30,31]. In particular, the band at 1320 cm\(^{-1}\) which arises from H–C–H wagging was very sensitive to the TPA\(^+\) conformations. At this Raman shift, the free TPA\(^+\) molecules would give a sharp band indicating the ideal S\(_4\) symmetry for free TPA\(^+\) ion. However, an additional band at 1338 cm\(^{-1}\) was observed in the spectra of all as-synthesized samples, suggesting that the TPA\(^+\) conformations did not maintain the ideal S\(_4\) symmetry, but rather twisted [30,31]. In ZSM-5 frameworks, TPA\(^+\) was occluded at the intersection of the straight (perpendicular to the (0k0) face) and zig-zag (perpendicular to the (h00) face) channels [33,34]. Thus, TPA\(^+\) conformation was altered to adapt the pore architecture of ZSM-5. Moreover, the portion of band at 1338 cm\(^{-1}\) compared to band at 1320 cm\(^{-1}\) of Ludox-ZSM-5 and RH-ZSM-5 was higher than that of RHC-ZSM-5, indicating more TPA\(^+\) occluded in the channel systems of ZSM-5 structure. These results also confirmed the ability of TPA\(^+\) to direct the formation of ZSM-5 structure, even in the reduced amounts used in this study.

After calcination, the hydrocarbon vibration bands at 750–1500 cm\(^{-1}\) were vanished showing the complete removal of OSDA from the ZSM-5 frameworks. Notably, it was observed the rise of a band at 290 cm\(^{-1}\) which was attributed to ten-membered rings or the pore-opening of ZSM-5 frameworks [30,31]. In the spectra of the as-synthesized samples, this band was overlapped by TPA\(^+\) vibration signal at 308 cm\(^{-1}\). In addition, RHC-ZSM-5 still exhibited the amorphous band at around 490 cm\(^{-1}\).

Fig. 6 shows TEM images of the products. As seen, Ludox-ZSM-5 and RH-ZSM-5 exhibited spherical shapes with rugged surface. The observed size was bigger than the calculated crystallite size, as obtained using Scherrer equation. This finding suggested that the observed ZSM-5 particles were an assembly of smaller ZSM-5 crystallites, which led to the formation of intercrystallite mesopores. The lattice fringes of these two samples were clearly observed confirming their crystalline nature. Distinct results were shown by RHC-ZSM-5, which was composites of ZSM-5 spherical particles
and disordered-mesoporous silica matrix. The latter was proven to be amorphous as shown by selected-area electron diffraction (SAED) pattern (Fig. 6i).

The textural properties of the products were evaluated using N₂ adsorption-desorption isotherm as depicted by Fig. 7a. The isotherms of Ludox-ZSM-5 and RH-ZSM-5 exhibited type-H₄ hysteresis behavior with a characteristic step down on the desorption branch at a relative pressure of ~0.4, corresponding to possible capillary condensation taking place in the mesopores. This kind of hysteresis behavior is commonly found in hierarchically porous zeolite [35]. N₂ adsorption-desorption isotherm of RHC-ZSM-5 is also provided in Fig. 7a. The isotherm exhibited type-H₁ hysteresis behavior which may be correlated to the networks of ink-bottle pores [35].

The textural properties of the products were provided in Table 1. As seen, the micropore volume, \( V_{\text{micro}} \) of Ludox-ZSM-5, RH-ZSM-5

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
<th>( S_{\text{ext}} ) (m² g⁻¹)</th>
<th>( V_{\text{tot}} ) (cm³ g⁻¹)</th>
<th>( V_{\text{micro}} ) (cm³ g⁻¹)</th>
<th>( V_{\text{meso}} ) (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludox-ZSM-5</td>
<td>352</td>
<td>90</td>
<td>0.24</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>RH-ZSM-5</td>
<td>349</td>
<td>100</td>
<td>0.24</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>RHC-ZSM-5</td>
<td>254</td>
<td>154</td>
<td>0.65</td>
<td>0.05</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\( ^a \) Determined using BET method.
\( ^b \) Determined using t-plot method.
\( ^c \) Determined at \( P/P_0 \approx 0.99 \).
and RH-ZSM-5 were 0.13, 0.12 and 0.05 cm$^3$ g$^{-1}$, respectively. For zeolites, ZSM-5 in particular, the micropores are strictly related to the crystal structure. Thus, the higher micropore volume, the more crystalline ZSM-5 have been synthesized. We observed similar correlation when comparing the ratio of $V_{\text{micro}}$ (0.12 cm$^3$ g$^{-1}$), $V_{\text{ext}}$, (154 m$^2$ g$^{-1}$) and total pore volume, $V_{\text{tot}}$, (0.65 cm$^3$ g$^{-1}$) than those of Ludox-ZSM-5 (90 m$^2$ g$^{-1}$ and 0.24 cm$^3$ g$^{-1}$, respectively) and RH-ZSM-5 (100 m$^2$ g$^{-1}$ and 0.24 cm$^3$ g$^{-1}$, respectively). The higher mesoporous character of RHC-ZSM-5 was related to the significant amount of amorphous part. Differently, since Ludox-ZSM-5 and RH-ZSM-5 were fully crystalline, those external surface area and mesopores volume values were completely originated from the crystalline ZSM-5. The large external surface area with high micropore volume showed the development of notable mesoporosity with preserved intrinsic microporosity of Ludox-ZSM-5 and RH-ZSM-5.

The NLDFT pore size distribution of Ludox-ZSM-5 exhibited a centered peak at around 3.5 nm. A similar feature was also exhibited by RH-ZSM-5 with a slight broad distribution from 5 to 15 nm. According to IUPAC, pores are classified based on their dimensional size, i.e. micro- (<2 nm), meso- (2–50 nm) and macropores (>50 nm) [36]. Thus, those NLDFT pore size distribution clearly showed the formation of mesopores in both Ludox-ZSM-5 and RH-ZSM-5. Generally, ZSM-5 solely contains its intrinsic uniform micropores with the size of ca. 0.55 nm [37]. The formation of mesopores, which have greater dimensional size than that of micropores, in such highly crystalline ZSM-5 is potential for increasing catalytic performance, especially for reaction with bulky molecules as reactants and/or products, due to the enhancement of molecular diffusion. Meanwhile, NLDFT pore size distribution of RHC-ZSM-5 showed a very broad peak ranging from 2 to 50 nm (Fig. 7b), which could be mesopores originated from the amorphous parts.

Fig. 8 depicts $^{29}$Si and $^{27}$Al MAS NMR spectra of the products. They were utilized to analyze the local coordination environment of silicon and aluminum. After deconvolution of $^{29}$Si MAS NMR spectra, four bands were observed at −118, −115, −110, and −103 ppm. The well-resolved band at 115 ppm and the shoulder at −118 ppm were corresponding to $Q_4$ (0Al) species. The band at 110 ppm was attributed to $Q_3$ (1Al) species. Furthermore, a broad band was observed at 103 ppm correlated to $Q_2$ species with a respective silanol group (Si(OSi)$_2$OH). For Ludox-ZSM-5 and RH-ZSM-5, the silanol groups presumably originated from the mesopores surface of zeolites. For RHC-ZSM-5, the proportion of $Q_2$ was found to be higher, as a contribution from the amorphous parts. All of the band assignments were in accordance with the previous reported $^{29}$Si MAS NMR spectra of ZSM-5 zeolites [38].

The $^{27}$Al MAS NMR spectra of RH-ZSM-5 supported the results in the $^{29}$Si MAS NMR spectra. In the $^{27}$Al MAS NMR spectra, two bands were observed at 56 and 0 ppm corresponding to tetrahedrally coordinated Al and octahedral extra-framework Al species, respectively. The Gaussian function was applied to fit the Al tetrahedral band. The information about the order of Al tetrahedral environment could be obtained from the FWHM values. The higher the value of FWHM, the less-ordered the Al tetrahedral environment [39,40]. The FWHM of Al tetrahedral band of Ludox-ZSM-5, RH-ZSM-5 and RHC-ZSM-5 were 7.1, 7.2 and 9.3 ppm, respectively. The less-ordered environment in RHC-ZSM-5 was due to the existence of Al tetrahedral in both zeolite and amorphous parts.

3.3. Plausible mechanism on the effect of silica structural properties

Based on the overall characterizations, we found that the reactivity of silica precursors to be transformed into crystalline ZSM-5 was related to Si–O–Si and Si–OH bonds, as illustrated in Fig. 9. In Ludox-ZSM-5 and RH-ZSM-5, less Si–O–Si bonds with considerable number of silanol groups were present which made them reactive to be crystallized into ZSM-5 phase. In the course of low-temperature synthesis, a great number of nuclei was formed and further assembled into spherical larger particles. This led to the formation of intercrystallite mesopores, as demonstrated by XRD, TEM and $N_2$ adsorption-desorption isotherm. During calcination, the hydroxyl groups in Si–OH bond underwent condensation with their adjacent hydroxyl groups resulting in the formation of more...
Si–O–Si bonds. This phenomenon led to the rearrangement of silica structure into a less-disordered structure. As a consequence, the resulted silica was less-reactive to be depolymerized into soluble silicates. Therefore, repolymerization step for remaking new Si–O–Si bonds around the OSDA, which would be further arranged and crystallized into zeolite phase, was difficult to achieve.

It was previously reported by Coppens and co-workers that TPA⁺ could play role as nontemplating structure-directing for the formation of disordered mesoporous silica network [22]. During the synthesis, TPA⁺ interacted with the surface of silica and further dragged together to fill the void in the silica mesopores in a piecemeal manner. The void filling by TPA⁺ would inhibit the agglomeration, thus, prevent the formation of dense silica to some extent. The void would later be mesopores after the removal of TPA⁺ through calcination. The non-templating structure-directing agent is a fairly common phenomenon involving various organic molecules, including TPA⁺, hexanediol, propylamine and ethanola- mine [22]. The part of RHC-ZSM-5, which was not transformed into ZSM-5 phase, might be directed into disordered mesoporous silica by TPA⁺. This ability of TPA⁺ might also help to assemble small crystallites to form hierarchically porous ZSM-5 in the synthesis of Ludox-ZSM-5 and RHC-ZSM-5 [18]. Clearly, it was shown that the structural properties of the natural silica source play a crucial role in the crystallization of ZSM-5 below 100 °C.

Fig. 8. (left) ²⁹Si and (right) ²⁷Al MAS NMR spectra of (a) RHC-ZSM-5, (b) RH-ZSM-5 and (c) Ludox-ZSM-5. The marginal offset of cumulative and deconvoluted spectra in ²⁹Al MAS NMR spectra were shifted downward for clarity.
4. Conclusions

Silica from rice husks was successfully extracted by applying sequential base-acid treatment. The silica is reactive to form ZSM-5 phase in the synthesis below 100 °C. The resulting ZSM-5 exhibits hierarchical porosity due to the presence of its intrinsic micropores (0.55 nm) and the additional intercrystallite mesopores (around 3.5 nm) originated from the spherical morphology of ZSM-5, which was composed of small crystallites. The reactivity of the rice husk silica was comparable to that of commercial silica source, i.e., Ludox HS-40. The subjection of silica into calcination process, prior to the synthesis, altered the silica structure through the condensation of hydroxyl groups. This phenomenon led the silica to be less-reactive in the synthesis of ZSM-5 below 100 °C. At this point, TPA+ may also play its nontemplating structure-directing ability for assisting the formation of disordered mesoporous silica matrix. Our results offered the possibility for implementing sustainable natural silica precursors in the low-temperature synthesis of hierarchical ZSM-5 below 100 °C. The insights about the effect of silica structural properties could be useful for further development of the synthesis of zeolite materials below 100 °C.

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