

Ultrasonic/microwave synergistic synthesis of well-dispersed hierarchical zeolite Y with improved alkylation catalytic activity

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Abstract—Well-dispersed hierarchical zeolite Y, structure-directed by ionic liquid 1-methyl-3-[3'-(trimethoxysilyl)propyl] imidazolium chloride, was synthesized for the first time using a novel ultrasonic/microwave synergistic synthesis (UMSS). The time required for the synthesis of zeolite Y by UMSS method was remarkably reduced to 6 h instead of 24 h under conventional hydrothermal conditions. The structures of all samples were characterized by XRD, BET, FT-IR, SEM and TEM. The results clearly demonstrated that the UMSS is a promising strategy to achieve zeolite Y with improved crystallinity, large BET surface area, bulky mesopore volume, well-dispersed morphology, small zeolite nanoparticle. The catalytic activity of hierarchically micro-mesoporous zeolite Y was evaluated by using the alkylation of *o*-xylene with styrene. Mesoporous zeolite Y synthesized by UMSS method showed significantly higher catalytic activity, stability and reusability, compared with conventional hydrothermal synthesis. It might be ascribed to its large mesoporous volume, small crystal nanoparticle and high surface area, minimizing the diffusion length as the reactant molecules diffuse into the pores, and correspondingly the products diffuse out of zeolites. This study suggests that UMSS method is a good alternative for the synthesis of micro-mesoporous zeolite Y, which may be of remarkable benefit for industrial applications.

Keywords: Micro-mesoporous Zeolite Y, Ionic Liquid, Ultrasonic/Microwave Synergistic Synthesis, Conventional Synthesis Method, Alkylation

INTRODUCTION

Zeolite Y is a faujasite-type zeolite with a tortuous and complex three-dimensional pore structure [1], which has been extensively applied in multiple industrial processes, such as hydrodesulfurization [2], aldol condensations [3], biochemistry [4], and petroleum refining [5]. However, the tiny pore characteristic (~ 7.4 Å) largely limits the diffusion of reactants to reach the active sites and reaction products to break away from the active sites, leading to the low catalytic efficiency [6,7]. An alternative method to increase the diffused efficiency involves introducing mesopores into zeolite [8]. The hierarchical zeolites thus obtained exhibit micropores and tailorable mesopores. The synergies of two channels can efficiently improve the accessibility of active sites through its mesopores, while maintaining the excellent hydrothermal stability of microporous molecular sieve [9-12].

Several strategies have been successfully employed to obtain hierarchical zeolites, such as post-processing [13], hard template method [14], and soft template method [15]. As far as we know, a large number of preparation methods have introduced substantial mesoporosity into zeolites, but these techniques show a certain degree

of defects. The post-processing method is usually time consuming, inefficient and too difficult to control, which may etch a majority of the unnecessary material resulting in the collapse of zeolites structure [16]. The mesopores formed by hard template cannot be modulated easily; their mesoporous structures mainly depend on the inherent porosity of temporary/sacrificial templates (artificial or biological) [17]. An alternative approach for the introduction of mesopores should therefore be attempted to avoid the disadvantages described above. In terms of design, soft templates of tunable dimensions, removable *via* calcination, would be an appropriate solution for the introduction of mesopores [18]. However, when considering the high cost, rarity of templates, the complexity and low yield of synthetic process, these factors still make them disadvantageous for industrial applications. Furthermore, researchers generally prepare molecular sieves by hydrothermal synthesis, which possess a very long crystallization time to acquire excellent crystals [19]. It is a significant drawback of the conventional hydrothermal synthesis, because of the increase in preparation costs at large scale production. Hence, what is most urgently needed now is to develop an alternative structure-directing agent with improved properties for template and a novel rapid synthetic method that can efficiently reduce synthesis time and to control nucleation and growth of zeolites.

Green chemistry is an emerging field that strives to protect human health and the environment [20]. Room-temperature ionic liquids (ILs) have attracted worldwide attention due to their potential as

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environmentally benign “green solvents” [21]. Moreover, they can play multiple roles in the synthesis of hierarchical materials, such as the template, solvent, and cosurfactant [22]. However, the general synthesis of ILs using conventional heating methods is a flawed process, which requires a great deal of time and energy. And it also needs large volumes of organic solvents to extract impurities during the purification process [23]. In view of the overwhelming interest in the applications of ILs to synthesize nanostructures, it is still a great challenge to develop an effective method to obtain an extremely cheap, abundant and environmentally friendly IL.

Ultrasonic is a source of high energy at a frequency range of 18–100 kHz, initiating reactive substances at the molecular level. The intense heat and pressure transmit to reactive substances by formation, growth, and collapse of cavity bubbles, thereby increasing the chemical reactivity of the reaction [24,25]. Zhou et al. [26] prepared hierarchical micro-mesoporous ZSM-5 with better surface area, pore size, larger pore volume, shorter induction time for nucleation and better catalytic activities by ultrasonic-assisted method in comparison with conventional hydrothermal method. Microwaves have ultra-high frequency electromagnetic wave in the range of 300 MHz–300 GHz [27]. Microwave heating is a process in which the materials themselves absorb microwave energy and then transform it into heat. In addition, microwaves almost pass through glass, plastic and porcelain without being absorbed. Thus, the reactions absorb microwaves only for self-heat, reducing energy consumption, improving physical and mechanical properties [28]. When compared with traditional heating, microwave heating can specially minimize the reaction time and largely increase the yield in the absence of solvent [23]. The small zeolite NaX nanoparticles with narrow particle size distribution, good crystallinity can be synthesized *via* the microwave heating method at relatively short processing times by control of the crystallization time and temperature [19]. UMSS method is ultrasonic coupling with microwave synthesis, which has absorbed the merits of the two energetic radiations, and may present many applicative values [29]. To the best of our knowledge, the production of micro-mesoporous zeolite Y by UMSS method has not yet been reported.

In this study, the mesoporous structure-directing agent of IL 1-methyl-3-[3'-(trimethoxysilyl) propyl] imidazolium chloride was synthesized by UMSS method (Fig. 1). Then the micro-mesoporous zeolites Y were successfully prepared by UMSS method and conventional hydrothermal synthesis using IL as a mesoporous structure-directing template. Our aim was to investigate the effect of various synthesis procedures on the crystal properties of hierarchical zeolite Y. The characteristics of the novel micro-mesoporous zeolites Y obtained from those two methods were fully investigated by a complementary combination technology. In addition, the micro-mesoporous zeolite Y, combining the advantages of mesoporous materials with intrinsic zeolite crystals, was expected to be

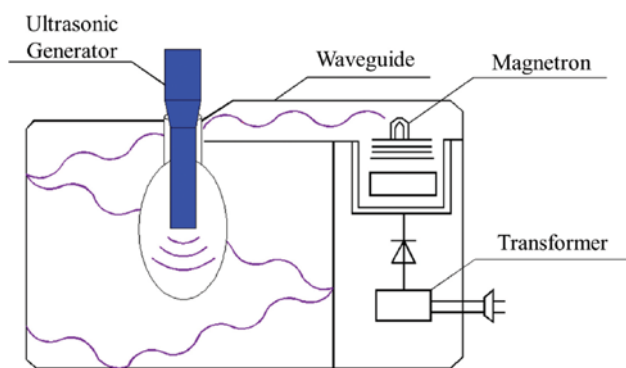


Fig. 2. Scheme of the ultrasonic/microwave synergistic method.

more suitable for applications in the alkylation of *o*-xylene with styrene as a catalyst, and its catalytic activity was thus investigated.

EXPERIMENTAL SECTION

1. Materials

1-Methylimidazole (99%), 3-chloropropyl trimethoxysilan (98%), sodium metasilicate (Na_2SiO_3 , SiO_2 44–47%), sodium aluminate (NaAlO_2), aluminum sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 99%), sodium hydroxide (NaOH , AR, 96%) were of analytical grade, and all were purchased from Aladdin. Deionized water was used in all experiment. All chemicals were used as received without further purification.

2. Synthesis of IL

IL 1-methyl-3-[3'-(trimethoxysilyl) propyl] imidazolium chloride was synthesized by UMSS method (Fig. 1). Experimental details and spectroscopic characteristic data of IL are given in the supporting information.

3. Synthesis of Micro-mesoporous Zeolite Y

Micro-mesoporous zeolite Y was synthesized by adding IL described above to conventional synthesis compositions for microporous zeolite Y, using both UMSS and conventional hydrothermal methods (Fig. 3).

3-1. Ultrasonic/Microwave Synergistic Synthesis

The precursor was prepared as follows: 0.36 g of NaOH , 10.99 g of Na_2SiO_3 and 0.82 g of NaAlO_2 were dissolved in 36.0 mL of deionized water, the solution was stirred at 50 °C for 1 h, followed by aging at 50 °C for another 5 h to obtain the precursor.

In a typical synthesis of micro-mesoporous zeolite Y: 15.38 g of Na_2SiO_3 was dissolved in 46.83 mL of deionized water. 9.45 g portion of the precursor was added dropwise into the solution and stirred thoroughly for 1.5 h at 50 °C. Then IL (water solution) was slowly dropwise added into the mixture. After the mixture was further stirred for 1.5 h, 0.18 g of NaOH , 3.49 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$,



Fig. 1. Scheme for successful synthesis of IL by UMSS method.

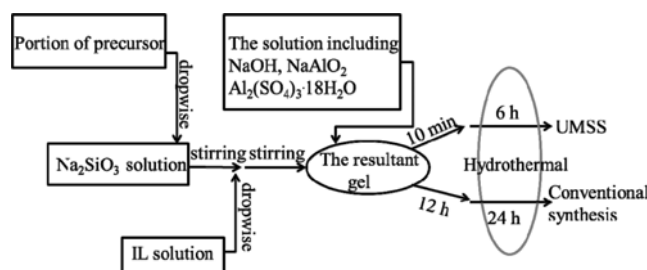


Fig. 3. Schematic representation of the procedure of micro-mesoporous zeolite Y synthesized by UMSS method and conventional synthesis route.

1.17 g of NaAlO₂ were added to the synthesis mixture under magnetic stirring. The resultant aluminosilicate gel had a molar composition of 1.0 Na₂O : 0.093 SiO₂ : 0.0087 Al₂O₃ : 21.86 H₂O : 0.15 IL. Then hydrothermal crystallization was then performed by UMSS or conventional hydrothermal method.

UMSS method was conducted as follows: the resultant gel was slowly poured into flat-bottomed glass flask and placed into ultrasonic/microwave synergistic instrument. The ultrasonic power was set as aforementioned. The microwave was irradiated at 200 W, reaction temperature was 80 °C and irradiation continued for a total of 10 min with a reverse duty cycle of 2 min. Eventually, a homogeneous milk white solution was observed, which was then transferred into a Teflon-lined autoclave and heated in an oven at 100 °C for 6 h (referred to as the crystallization time). The crystallization products were collected by filtration, dried at 100 °C in an air, and calcination was carried out with a heating rate of 3 °C·min⁻¹, then kept at the target temperature 600 °C for 5 h to remove the template. The final product was denoted as Y(UMSS).

3-2. Conventional Synthesis Method

The synthesis procedure was the same as that of UMSS method except the “ultrasonic/microwave radiations step” and crystallization time, whereby the 10 minutes of ultrasonic/microwave radiations had been replaced by further stirred at 50 °C for 12 h and the crystallization time was lengthened to 24 h. The final product was named as Y(C).

4. Catalysts Preparation

To decrease the Na content of zeolite Y and thus increase its acidity, H⁺ was used for ion-exchange of Na⁺ in zeolite NaY. The H-form samples of zeolite Y were obtained by repeated procedure of ion exchange with 1 M NH₄Cl solution at 90 °C for 4 h, and then samples were converted to the H⁺ form *via* calcination in air at 550 °C for 6 h and denoted as HY(UMSS), HY(C), respectively.

5. Catalytic Tests

The alkylation reactions were carried out in a continuously stirred oil batch reactor under reflux conditions. 5.89 g of styrene, 45 g of *o*-xylene (molar ratio of *o*-xylene to styrene is 7.5 : 1) and 1.00 g of catalyst were introduced in a 100 mL three-neck round-bottom flask equipped with a condenser at 120 °C for 3 h. One third of *o*-xylene were added to the round-bottom flask, followed by the desired amount of catalyst, then the mixture of 5.89 g of styrene and the remaining *o*-xylene was dropwise added into the flask for 2 h. The final reaction mixture remained for another 1 h. After the reaction, unreacted *o*-xylene was distilled out under atmo-

spheric pressure. Then the obtained liquid was denoted by crude product, which was analyzed with GC-9890A gas chromatograph equipped with OV-1 capillary column and a flame ionization detector (FID). The yield of PXE was defined as follows:

$$\text{yield of PXE (\%)} = \frac{\text{actual product weight}}{\text{theoretical product weight}} \times 100\%$$

6. Characterizations

Fourier transform infrared spectra (FT-IR) of samples were recorded on a Bruker Tensor 27 (German) using DRIFT techniques, scanned from 4,000 cm⁻¹ to 500 cm⁻¹. The sample was smeared on a KBr substrate. The samples were evacuated at 100 °C for 4 h before the measurement. ¹H NMR and ¹³C NMR spectra were performed on an AvanceII 200 spectrometer (Bruker), using CDCl₃ as a solvent. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (Germany) system equipped with Cu-Kα radiation (operation at 40 KV, 30 mA). And the XRD patterns were collected in the range of 3-50° in 2θ/θ scanning mode with a 0.02° step and scanning speed of 10°/min. Transmission electron microscopy (TEM) experiments were conducted on a JEM-1230 microscope operated at 100 kV. The samples for the TEM measurements were dispersed in ethanol ultrasonically and were supported on a Cu grid. Scanning electron microscope (SEM) images were recorded on a Hitachi S-3400N SEM at an acceleration voltage of 20 kV. Samples were fixed using a conductive carbon double-sided sticky belt. The nitrogen adsorption and desorption isotherms were measured with an ASAP-2020 (Micromeritics USA) at 77 K. The samples were out gassed for 6 h at 350 °C before the measurements. The specific surface area (*S*_{BET}) was determined from the linear part of the Brunauer-Emmett-Teller BET equation (*P*/*P*₀=0.05-0.25). The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the N₂ isotherm. The total pore volume (*V*_{total}) was estimated from the amount of nitrogen adsorbed at a relative pressure (*P*/*P*₀) of ca.0.995.

RESULTS AND DISCUSSION

1. Characterization of Hierarchically Micro-mesoporous Zeolite Y

To compare the zeolites synthesized by the UMSS method with those obtained by the conventional synthesis process, the XRD (Fig. 4) was applied to analyze the crystal structures. The XRD patterns of these synthesized samples exhibit well-resolved peaks in the high 2θ region of 3-50°; the peak positions are nearly identical. And the high-angle XRD peaks are characteristic of the crystalline structure of zeolite Y [30-32]. As for the two samples, the reflections from the sample Y(UMSS) are obviously sharper and the corresponding intensity are higher than sample Y(C), which is attributed to the higher crystallinity of the sample Y(UMSS). It is demonstrated that ultrasonic and microwave can provide a high energy for the formation of zeolite, so that it is easier to crystallize even in the shorter crystallization time.

Fig. 5 clearly shows that both two samples exhibit a broad peak in the low 2θ region of 0.5-5°, suggesting the formation of uniform mesoporous structures in zeolite Y [15]. These results provide abun-

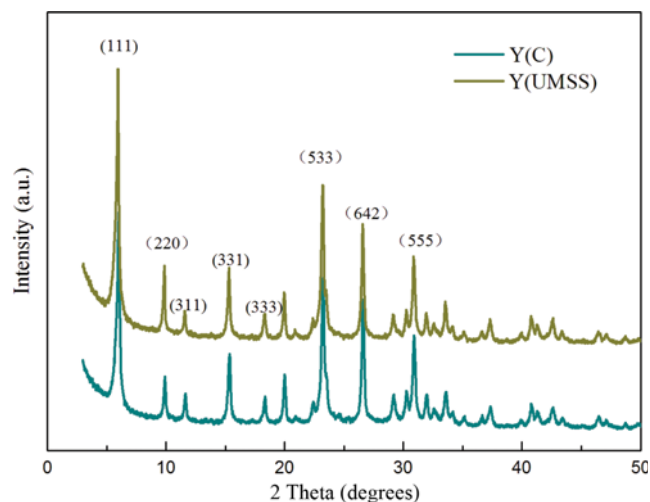


Fig. 4. Power X-ray diffraction patterns in the high 2θ region of samples Y(UMSS) and Y(C).

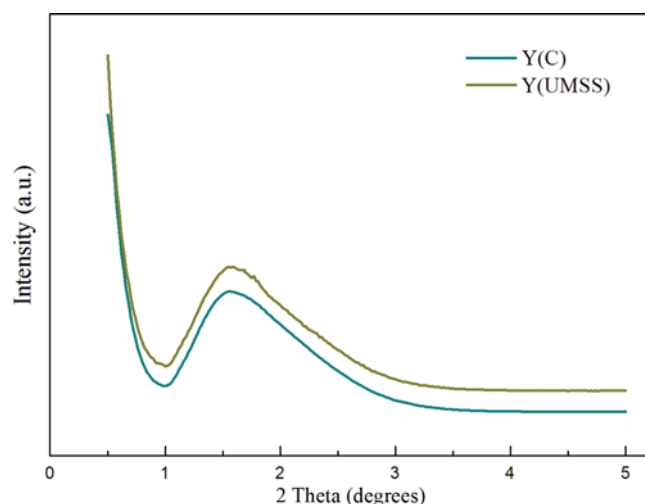


Fig. 5. Small-angle XRD patterns for samples Y(UMSS), Y(C).

dant proof that hierarchically micro-mesoporous zeolite Y can be facily synthesized *via* UMSS method.

Fig. 6 shows the IR spectra of the samples synthesized by UMSS method (a), conventional synthesis route (b). The peak positions of the two samples are nearly synonymous. The as-synthesized samples have broad bands around 469 cm^{-1} which can be assigned to deformational vibration and symmetric vibration of $-\text{Si}-\text{O}-\text{Si}-$ and $-\text{Al}-\text{O}-\text{Al}-$ bonds. The band at 572 cm^{-1} appears which is attributed to the presence of double six-member rings in zeolite Y, suggesting the nature of primary and secondary structural building units [1]. These results provide an obvious evidence for the formation of the zeolite Y obtained by UMSS method in a short crystallization time.

The N_2 adsorption-desorption isotherms for both samples (Fig. 7(a)) show representative hysteresis loops of type IV. Each has an obvious well-defined step at relative pressure of 0.4–0.8, which is attributed to a characteristic of mesoporous structure in those samples [11,33]. Meanwhile, the adsorption amount of nitrogen at the

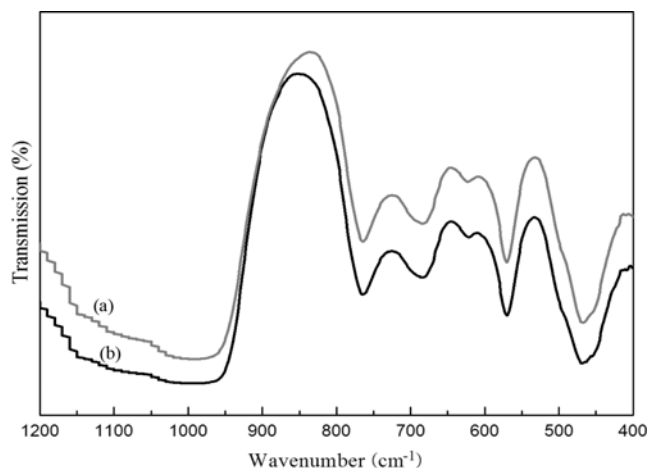


Fig. 6. FT-IR spectra of two sample: (a) Y(UMSS), (b) Y(C).

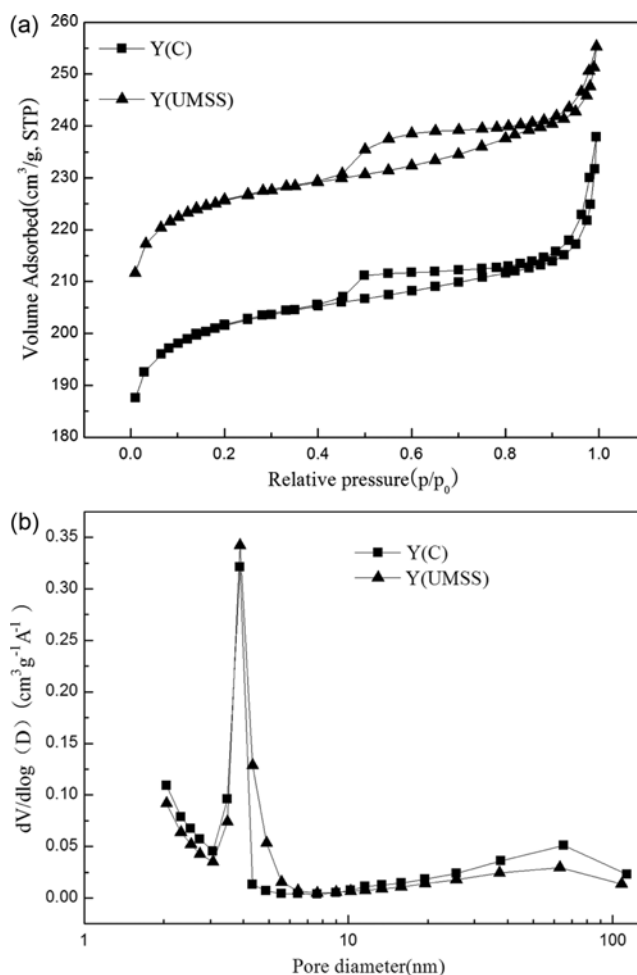


Fig. 7. N_2 adsorption-desorption isotherms of samples were obtained *via* UMSS and conventional hydrothermal method (a); the corresponding pore size distributions of those samples (b).

lower relative $P/P_0=0-0.1$ implies the presence of micropores in zeolites [34]. It can be clearly seen from Fig. 7(b) that the mesoporous size is around 3.89 nm and the pore distribution of the

Table 1. Textural and structural properties of the synthesized micro-mesoporous zeolite Y by different methods

| Sample | S_{BET}^a ($m^2 \cdot g^{-1}$) | S_{ext}^b ($m^2 \cdot g^{-1}$) | V_{meso} ($cm^3 \cdot g^{-1}$) | V_{total} ($cm^3 \cdot g^{-1}$) | Pore size ^c (nm) |
|---------|---------------------------------------|---------------------------------------|---------------------------------------|--|--------------------------------|
| Y(C) | 672 | 74 | 0.09 | 0.37 | 3.89 |
| Y(UMSS) | 752 | 70 | 0.12 | 0.40 | 3.89 |

^aBET method^bt-Plot method^cBJH model applied to the desorption branch of the isotherms

sample Y(UMSS) is larger than Y(C). From the physicochemical properties summarized in Table 1, note that the surface area and pore volume of the sample Y(UMSS) are also increased, compared with the sample Y(C). Notably, the sample Y(UMSS) exhibits a BET surface area of $752 m^2 \cdot g^{-1}$, in the case, $70 m^2 \cdot g^{-1}$ is from the external surface and the mesopore volume is increased to $0.12 cm^3 \cdot g^{-1}$. Ultrasonic can affect reactive substances at the molecular level so that the templates ILs are evenly dispersed in the conventional composition of zeolite Y to form more mesoporous channels at 3.89 nm than conventional hydrothermal synthesis. It also can be displayed from the images of TEM (Figs. 8(a) and (b)). These results demonstrate that the hierarchical zeolites Y were successfully syn-

thesized *via* UMSS method in a short crystallization time of 6 h.

The presence of micropores and mesopores can be directly inferred from the TEM images (Figs. 8(a) and (b)). The mesopores are both present in good agreement between the neighboring microporous frameworks (the mesopores in the crystal are marked by black lines), forming the hierarchical structure of the zeolite Y. Moreover, the diameters of wormlike mesostructures vary through the mesoporous channels and the mesoporous channels are not straight, which may be ascribed to the aggregation of template IL. The phenomena suggest that intracrystalline mesoporosity could be formed through the sequential anchoring and templating mechanism of ILs.

The SEM images show that micro-mesoporous zeolites Y both have similar morphology (Figs. 8(c) and (d)). The primary particles are schistose block and aggregate to form cauliflower-like. The presence of physically separated amorphous mesoporous crystals was not detected throughout the entire sample. The sample Y(C) shows closer cauliflower-like structure sized at ca. $0.85 \mu m$ with many macropores present between the particles, which introduce some macropores at about 65 nm (Fig. 7(b)). Whereas, UMSS method shortens the crystallization time and consequently decreases excessive crystal growth rate and reduces the aggregation rate [35]; thus the sample Y(UMSS) exhibits well-dispersed cauliflower-like morphology at ca. $0.81 \mu m$. Also, the particle size distribution of zeolite

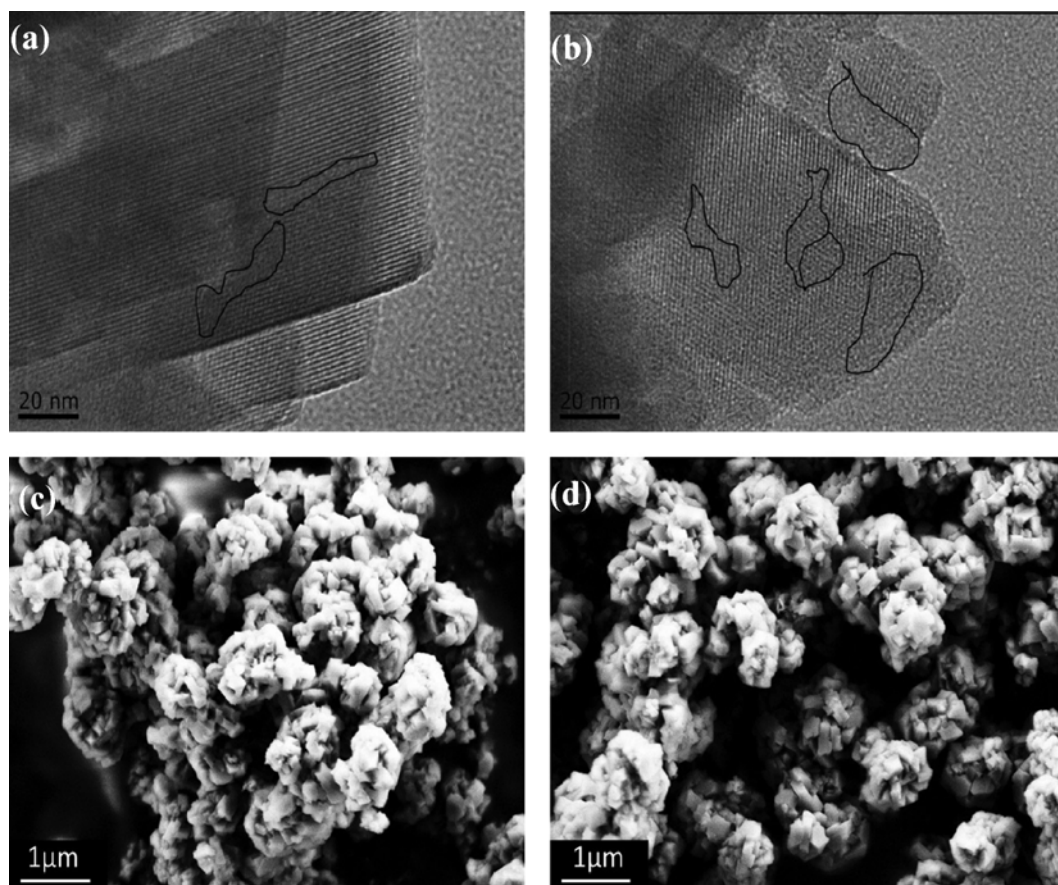


Fig. 8. TEM images of the novel micro-mesoporous zeolite Y synthesized by the conventional heating (a), the UMSS method (b) (the mesopores in the crystal are marked by black lines). The SEM images of samples Y(C) (c) and Y(UMSS) (d).

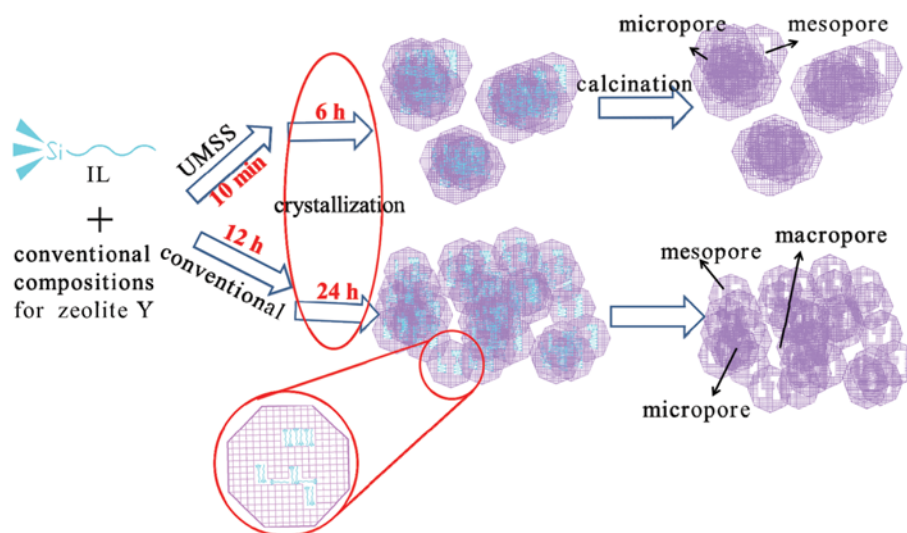


Fig. 9. Schematic representation of phase transformation detected by XRD, SEM and TEM during the conventional hydrothermal synthesis and UMSS method of micro-mesoporous zeolite Y using IL as a template.

Y(UMSS) are visually more uniform than the conventionally heated zeolites. Such dispersed cauliflower-like morphology and small zeolite nanoparticle minimize the diffusion length of reactant molecules into the pores and correspondingly the products out of zeolites. Thus, it is believed that the hierarchic sample Y(UMSS) has a potential for the high adsorption ability or the superior catalytic activity in the reaction involving large molecular species.

A mechanism is proposed in the synthesis of micro-mesoporous zeolite Y by UMSS method. The UMSS method and IL 1-methyl-3-[3'-(trimethoxysilyl) propyl] imidazolium chloride are played essential roles in the crystallization stage. The results of this research show that the formation of mesoporous channels could be ascribed to the hydrolyzing and anchoring of the template IL. The head groups $(\text{CH}_3\text{O})\text{-Si-}$ hydrolyze to -Si-OH and attract the conventional composition synthesis of zeolite Y to form -Si-O-Si- , -Si-O-Al- bonds. Moreover, the electrostatic interaction between the positively charged imidazole head group and negatively charged aluminosilicate gels plays an important role in the formation of mesopores. Like the case of zeolite synthesis, the organic tail of IL directs the mesoporous channels, while the silica moiety is incorporated in the resultant aluminosilicate frameworks. Therefore, mesoporous channels are constructed with crystalline microporous zeolite Y by calcination to eliminate the ILs. Microwave heating enhances the dissolution of the gel precursors, consequently raising the nucleation and crystallization rate of zeolite Y. Correspondingly, zeolites with small crystal nanoparticle, large surface area as well as high crystallinity are synthesized. In addition, the intense heat and pressure transmit to reactive substances by formation, growth, and collapse of cavity bubbles with the assistance of ultrasonic. It can form acoustic cavitation phenomenon which can shear the reunion and reduce the particle size. At the same time, the ultrasonic can largely enhance mass transfer to promote a chemical reaction. Thereby the template IL is evenly dispersed in the conventional composition of zeolite Y to the formation of more mesoporous channels at 3.89 nm. Hence, in the presence of IL, UMSS method can easily synthesize micro-

Table 2. Catalytic stability of the HY(UMSS) and HY(C) catalysts in the alkylation of *o*-xylene with styrene

| <i>O</i> -Xylene | Styrene | Phenylxylyl ethane(PXE) | | |
|------------------|---------|-------------------------|------|------|
| Catalyst/Run | 1 | 2 | 3 | 4 |
| HY(UMSS) | 91.2 | 89.4 | 88.1 | 85.6 |
| HY(C) | 82.1 | 76.3 | 70.0 | 65.1 |

mesoporous zeolite Y with well-dispersed morphology and small particle size in a shorter crystallization time.

2. Catalytic Activity

To investigate the effect of the facile diffusion in the micro-mesoporous zeolite Y on catalytic performance, alkylation of *o*-xylene with styrene over the HY(C) and HY(UMSS) catalysts was chosen as a probe reaction to discover their differences. In this reaction, the sample HY(UMSS) shows a higher catalytic activity compared with HY(C) (Table 2). It can be attributed to its large mesoporous volume, small crystal nanoparticle and the relatively high surface area.

Stability and reusability of the catalyst are significant for any catalytic system. Note that the deactivation of HY(C) lost is much faster and its PXE yield dropped to 65.1% after the fourth recycling experiments. However, only 5.6% reduction in the activity was observed even after four runs with the HY(UMSS) catalyst. The outstanding durability of the HY(UMSS) catalyst can be attributed to the reality that ultrasound/microwaves enhance the stability of the mesoporous structure. These results show that the UMSS method is applicable for the improvement of catalytic activity and stability of HY.

CONCLUSIONS

Well-dispersed hierarchical zeolite Y was successfully synthesized using IL as a mesopore director by a novel UMSS method for the first time. Compared with conventional hydrothermal synthesis, the UMSS method not only makes productive process inexpensive, facile, scalable, and controllable, but also produces zeolites with large surface area, bulky pore volume as well as excellent crystallinity with hydrothermal time of 6 h. Besides, the sample Y(UMSS) has well-dispersed cauliflower-like morphology with short diffusion path length; thus reactants diffuse easily into the pores, and correspondingly the products also diffuse out freely. Therefore, HY(UMSS) exhibits a high product yield and long catalytic life in the alkylation of *o*-xylene with styrene. Accordingly, it is concluded that the UMSS method can open the way to industrial synthesis of ionic liquids and micro-mesoporous zeolites.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Ultrasonic/microwave synergistic synthesis of well-dispersed hierarchical zeolite Y with improved alkylation catalytic activity

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATIONS OF STRUCTURE-DIRECTING AGENT

1. Synthesis of IL

Raw materials 1-methylimidazole (0.265 mol) and 3-chloropropyl trimethoxysilane (0.265 mol) were used to prepare 1-methyl-3-[3'-(trimethoxysilyl) propyl] imidazolium chloride ionic liquid (IL) by UMSS method (Fig. 1). The two mixtures were poured into a reaction vessel, and then placed into a microwave oven equipped with ultrasonic. The ultrasonic power was set at 300 W with a cycle of working 1.1 S and intermitting 1.1 S. The mixture was irradiated at 320 W, reaction temperature was 120 °C and irradiation continued for a total of 2 min. Then the ionic liquid was directly dried under continuous evacuation (1 mm Hg) at 100 °C for 12 h without any purification. After cooling to room temperature, the product was obtained as yellowish viscous liquid in 100% yield, which was stored under dry conditions.

2. Results of Characterization

FTIR (KBr) spectrum for the IL is shown in Fig. S1. The absorption peaks at 3,300-2,800 cm⁻¹ are characteristic to different C-H bond stretching vibrations. The band appearing at 3,153 cm⁻¹

and 3,088 cm⁻¹ can be attributed to C-H bond stretching of the imidazole ring. The band occurring at 1,566 cm⁻¹ can be ascribed to C=C bond stretching of the imidazole ring. The peak at 1,638 cm⁻¹ corresponds to C-O bond stretching. The peak position at 1,180 cm⁻¹ is assigned to be stretching vibrations of H-C-N of imidazole ring. Both samples exhibit peak at 1,081 cm⁻¹, which indicates the presence of Si-O. The peak at 620 cm⁻¹ emerges, attributing to the stretching vibrations of C-N-C of imidazole ring [1].

In Fig. S2(a) ¹H NMR (CDCl₃): δ=10.412 (s, 1H, -N-CH-N-),

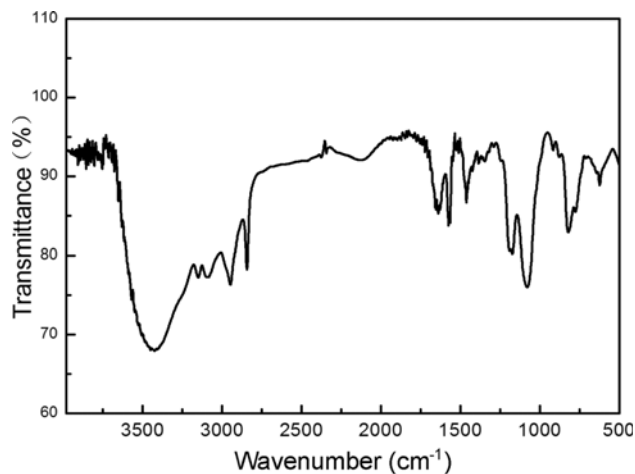


Fig. S1. FT-IR (KBr) spectrum of IL.

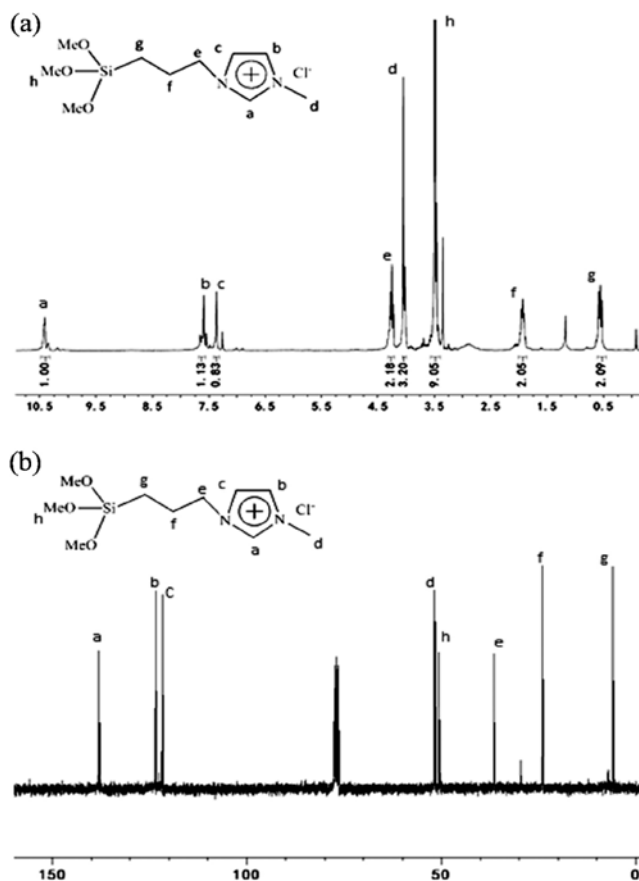


Fig. S2. (a) ¹H NMR spectrum of IL, (b) ¹³C NMR spectrum of IL.

7.591 (s, 1H, -N-CH=CH-N-), 7.366 (s, 1H, -N-CH=CH-N-), 4.25 (t, 2H, -N-CH₂-), 4.0 (s, 3H, -N-CH₃), 1.9 (quint, -CH₂-CH₂-CH₂-), 3.433 (t, 9H, -Si-OCH₃), 0.5 (t, 2H, -Si-CH₂-).

In Fig. S2(b) ¹³C NMR (CDCl₃): δ=138.01 (-N-CH-N-), 122.43 (-N-CH=CH-N-), 121.73 (-N-CH=CH-N-), 36.498 (-N-CH₂-), 51.652 (-N-CH₃), 24.069 (-CH₂-CH₂-CH₂-), 5.885 (Si-CH₂-), 50.625 (-Si-OCH₃) [2]. Those results show a striking evidence for the syn-

thesis of IL.

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