Contents lists available at SciVerse ScienceDirect



### Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jalcom

# Competition balance between mesoporous self-assembly and crystallization of zeolite: A key to the formation of mesoporous zeolite

### Hua Li<sup>a,1</sup>, Huazhong Wu<sup>b</sup>, Jian-lin Shi<sup>c,\*</sup>

<sup>a</sup> Department of Inorganic Materials, College of Chemistry Chemical Engineering and Materials Science, Soochow University, 199 Renai Road, Suzhou 215123, Jiangsu Province, PR China

<sup>b</sup> Department of Chemistry and Chemical Engineering, MinJiang University, Fuzhou 350108, Fujian Province, PR China

<sup>c</sup> State Key Lab of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 DingXi Road, Shanghai 200050, PR China

#### ARTICLE INFO

Article history: Received 9 November 2012 Received in revised form 20 December 2012 Accepted 20 December 2012 Available online 29 December 2012

Keywords: Hierarchical porous structure Mesoporous materials Zeolites Kinetics Competition balance Heterogeneous catalysis

#### ABSTRACT

A hierarchical meso-/microporous aluminosilicate has been synthesized through kinetic control over the competition balance between mesoporous self-assembly and microporous zeolite crystallization by using hexadecyl trimethyl ammonium bromide (CTAB) and tetrabutylammonium hydroxide (TBAOH) as mesoand micro-porogens, respectively. A very small pH value range of 11.10–11.30, which can be well tuned by added ethanol volume fraction and/or NaOH addition, was found to be suitable for the formation of mesoporous zeolite without phase separation. Balanced inorganic species adsorptions onto the mesoand micro-colloids are discussed and proposed to be the two key underlined mechanisms in the successful synthesis. The material shows perfect crystallization of zeolite frameworks and relatively high surface area and meso-/micropore volumes. The prepared mesoporous zeolite showed much higher catalytic activity in the reaction between lauric acid and ethanol than those when using both amorphous mesoporous materials and conventional ZSM-5 zeolite as catalysts.

© 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

A series of crystalline microporous aluminosilicates, e.g., ZSM-5 type zeolites, are widely used in catalysis, separation and environmental fields [1,2] due to their high hydrothermal stability and strong solid acidity. The catalytic activity of zeolite, however, is inevitably subject to the diffusion limitations of bulky reactants/ products in their micropore systems (typically smaller than 1.2 nm), especially in the reactions involving macromolecules [3,4]. To solve this problem, the introduction of nanosized pore network into the zeolites may help. Thus, the synthesis of hierarchically porous zeolites has attracted extensive attentions among material and catalysis researchers.

To date, a number of promising strategies have been developed for synthesizing hierarchically porous zeolites, most of which were mesoporous zeolites. These approaches can be summarized briefly as follows: (1) dealumination or sequential desilication–dealumination [5,6] which involves post-etching of intact zeolites to generate mesoporosity; (2) crystallization of the framework of pre-

\* Corresponding author. E-mail addresses: lihua123@suda.edu.cn (H. Li), jlshi@sunm.shcnc.ac.cn (J.-l. synthesized mesoporous aluminosilicates [7,8], typically the steaming-assisted crystallization methods; (3) the assembly of nanosized zeolite crystallites [9], in which the mesopores were formed among the crystallites. Generally, in later two routes, tet-rapropylammonium (TPAOH) or tetrabutylammonium hydroxide (TBAOH) was commonly used as micropore structure-directing agent (SDA) for ZSM-5 zeolites while various hard or soft templates were used as mesoporogens. By using hard templates, such as various carbon materials and mono-disperse polystyrene (PS) spheres, complicated multi-steps were usually involved due to the incompatibility between hard substrates and precursor species [10], and in some cases isolated secondary porosity would form, which was inapplicable for the diffusion of large molecules [11].

In recent years, some kinds of soft templating methods [10,12,13] including cationic or silylated polymer and amphiphilic organosilane have been successfully employed as templates in generating hierarchical structures without phase separation between the mesophase and crystalline zeolite. For example, stable single-unit-cell nanosheets of zeolite MFI [14] were firstly fabricated with a specially designed di-quaternary ammonium-type surfactant (C<sub>22-6-6</sub>), in which diammonium head group acted as an effective structure-directing agent for the MFI zeolite and the hydrophobic interaction between the long-chain tails induced the formation of mesoscale micellar structure. These routes, unfortunately, required

Shi).

<sup>&</sup>lt;sup>1</sup> Tel./fax: +86 512 65880089.

<sup>0925-8388/\$ -</sup> see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2012.12.111

uniquely designed templates, which were synthesized by very complex processes and unavailable on market up to date.

In contrast to the special template above mentioned, it would be facile to prepare hierarchical zeolites by using ordinary surfactants as the mesoporogens, such as hexadecyl trimethyl ammonium bromide (CTAB) [15,16]. However, synthetic strategy using ordinary surfactant template still remains a great challenge in synthesizing mesoporous zeolites: either phase separation between meso- and micro-phases or non-crystallization of the framework was almost unavoidable. The failure in the synthesis of mesoporous zeolite using conventional soft templates has been mainly attributed to the weak binding between these soft templates and silicate species [17–19]. In addition to this, the size and property of zeolite seeds [11,20,21] were also found to be an important factor. For example, last year, our group reported that the aging time of zeolite seeds could strongly influence the synthesis of hierarchical porous zeolite in a hydrothermal route in which zeolite seed size was found to be a key factor responsible for the mesoporous zeolite by matching CTAB-assisted mesostructure formation and zeolite crystallization [11]. In such a report, ethanol was added to the reaction mixture to stabilize those zeolite seeds. In a word, as the crystallization of zeolites is kinetically a very slow process compared with the rapid formation of the mesoporous phase at low temperature while a rapid crystallization happens once it reached a relatively high temperature (usually 150 °C for ZSM-5), therefore, a mismatch between kinetics and thermodynamics will easily result in the failure in the fabrication of mesoporous zeolites.

Apart from the synthetic factors mentioned above, the phase separation may possibly happen from the beginning of synthesis. From the kinetic point of view, there are two factors which need to be addressed. First one is the adsorption competition: mesotemplates (for example, CTAB micelles) and microtemplates (for example, TPAOH) would compete with each other to adsorb silicate species (namely, adsorption competition), which would result in phase separation once two kinds of porogens were mixed together. If mesotemplates are more attractive to silicate species than microtemplates, the silicate species previously adsorbed on the microtemplates would tend to be desorbed from them and transfers onto mesotemplates. As a result, mesoporous phase with non-crystalline framework would be achieved. In contrast, the crystalline microporous zeolites without intracrystal mesoporous structure could be obtained. If the conditions were in between the above two extreme cases, either a mixture of zeolite crystal and mesophase, or well-crystallized mesoporous zeolite would be obtained, which was decided by the competition balance between these two adsorption competitions. The second one is colloid interaction. The interaction between two kinds of organic/inorganic composites, i.e., meso-colloids of silicate species adsorbed onto mesotemplates, (i.e., CTAB micelle/inorganic composite colloid) and micro-colloids of silicate species adsorbed onto microtemplates (i.e., TBAOH/inorganic composite colloid), respectively, would decide whether the phase separation would happen or not in the final product. Two organic/inorganic composite colloids may have different surface charges due to different pH value or zeta potential when silicate species were adsorbed onto different porogens. The phase separation would not happen under the condition that the electrostatic repulsion between two kinds of composite colloids was so low as not to separate them with each other. As the pH value, i.e., Zeta potential plays a decisive role in modulating the electrostatic repulsion/attraction, therefore, it is highly valuable to explore the relationship between the formation of mesoporous zeolite and pH value.

Recently, we reported a simple route to synthesize the hierarchical porous zeolite [16]. Our process started from the synthesis of zeolite seeds solution by using TBAOH as microtemplate, and then a mesoscale self-assembly process was applied to allow the amorphous zeolite seeds further assemble with each other to form mesoporous zeolite precursor by using CTAB as mesotemplate and ethanol as additive. And the final hierarchical porous zeolite was obtained through a steam-assisted crystallization (SAC) method. However, the synthesis was found very sensitive to experimental parameters, which was similar to most of literature reports. It is important to find the underlined key factors affecting the successful synthesis of mesoporous zeolites. In the present work, we report our findings of the key factor governing the competition between mesoporous self-assembly and crystallization of zeolite through adjusting the amount of used ethanol and pH value, and the balanced inorganic species adsorption competition onto the meso- and microtemplates and electrostatic interaction between meso- and microtemplate-based colloids were proposed to be the underlined mechanisms responsible for the formation of mesoporous zeolite.

#### 2. Experimental

#### 2.1. Materials synthesis

Sample Hp-E was prepared according to the procedure which was described elsewhere (Hp-ZSM) [16], however, with lots of improvements. Briefly, three independent steps were involved in the synthesis of Hp-E: first, the synthesis of amorphous zeolite seeds in aqueous solution, second, mesoscale self-assembly among zeolite seeds as inorganic source and CTAB as mesotemplate using ethanol and distilled water as mixed solvent, and finally, the steam-assisted crystallization by employing the dried meso-/micro-amorphous materials as precursor. Hp-Na was prepared similar to Hp-E but with NaOH (0.9 ml, 0.5 mol/L aqueous solution) being added to adjust pH value. The factors influencing the final structure, including the amount of ethanol and pH value, were investigated. Herein, according to the above synthetic conditions, the products were named respectively as Hp-E(X) and Hp-Na(X), here E and Na are the abbreviations of ethanol and NaOH, respectively, while X refers to the volume (ml) of ethanol in the mixing solution.

The synthesis of wet gel was basically the same as in the previous report and the whole stirring process was carried out at 35 °C. The zeolite seeds solvent was statically aged at room temperature for 24 h. Therein, the molar ratios of the dried gel mixture were Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:Na<sub>2</sub>O:TBAOH:CTAB = 0.017:1:0.017:0.153:0.099 for Hp-E(X) and Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:TBAOH:CTAB = 0.017:1:0.025:0.153:0.099 for Hp-Na(X), respectively. During all reactions, the total volume was kept at 21 ml by using EtOH and H<sub>2</sub>O as mixed solvents and the amount of TEOS was fixed at 0.66 mol/L. All of the gels were dried at 50 °C. The dried gel was steaming-thermally treated at 155 °C for 40 h. Afterwords, the products were washed repeatedly with distilled water, dried at 100 °C and then calcined at 550 °C for 6 h to remove the organic agents. The effects of pH value and ethanol were the focuses of this study.

The synthetic process of ZSM-5 was synthesized using conventional hydrothermal route, in which the mixed sol of precursors was stirred to form a gel, then aged at ambient temperature and finally, hydrothermally theated at 155 °C for 72 h.

#### 2.2. Characterization

Powder XRD patterns were recorded by using a Rigaku D/Max 2200PC diffractometer with Cu K $\alpha$  radiation (40 kV and 40 mA) with a scanning rate of 0.6 min<sup>-1</sup> for small-angle testing and 10° min<sup>-1</sup> for large-angle testing. The N<sub>2</sub> sorption isotherms were measured using Micromeritics ASAP 2020 porosimeters at 77 K. The mesoporous specific surface area, pore-size distribution, and pore volume were calculated using the Brunauner–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore specific surface area and volume were calculated by the *t*-plot method. FE-SEM (field-emission-scanning electron microscopy) analysis was performed on a Hitachi S4800 electron microscope. TEM images were obtained on a JEOL-2010F electron microscope operated at 200 kV.

#### 2.3. Catalytic reaction

The catalytic reactions were carried out in a three-necked round bottom flask equipped with a reflux condenser  $(351 \pm 2 \text{ K})$ , a thermometer and a sampling system. The whole system was kept in an oil bath, which was placed upon a magnetic stirrer. A certain amount of lauric acid and ethanol to form totally 5 ml mixture with the molar ratio between lauric acid and ethanol fixed at 1:4. Then, 0.1 g catalyst was added into the mixture. The yield of ethyl laurate was determined periodically by using GC–MS (Agilent, 6890/5973 N).

#### 3. Results and discussion

As discussed above, the phase separation could happen from the beginning of reaction, depending on different experimental parameters. In our experiments, pH value was primarily explored since it would affect the aggregation of mesotemplates, zeta potential in the mixed system and the electrostatic interaction among the templates and inorganic species.

#### 3.1. Effect of ethanol volume on pH value in the reaction system

The relationship between the pH value and the ethanol adding amount under the presence (Hp-Na) and absence (Hp-E) of NaOH, and also the phase diagram for the mesoporous zeolite formation, were given in Fig. 1. The pH values of every sample can be found according to their ethanol volumes indicated in the sample names. It can be seen that the pH value increases with the increase of ethanol amount for both Hp-E(X) and Hp-Na(X). The pH values for all Hp-Na(X)-type samples are higher than those of Hp-E(X) at the same amount of ethanol added due to the addition of NaOH. The shaded area was found in this study to be a zone in which mesoporous zeolite could be obtained. Apart from this area, as we found in this report, only phase-separated mixture of zeolite crystals and amorphous mesophase, or amorphous mesoporous materials could be observed. The pH value for the formation of microporous zeolites was also indicated at 11.9 in the figure.

Table 1 lists the textual properties of the successfully synthesized mesoporous zeolites in the shaded area in Fig. 1. The peak pore size decreased with the increasing ethanol amount from 2.54 nm for Hp-E(10) to 1.95 nm for Hp-E(13) of Hp-E series and from 2.23 nm for Hp-Na(0) to 1.65 nm for Hp-Na(7) of Hp-Na series, respectively. The relative percentages of microporous volume ( $V_{mic}/V_{total}$ ) were calculated and are also listed for comparison (Table 1). Similar to the literature repot in which the amount of ethanol was found to decrease microporous volume percentage in hydrothermal route [11], the present research also demonstrated that ethanol had influenced the microporous properties significantly:  $V_{mic}/V_{total}$  decreased apparently at the increased amount of ethanol after NaOH was added into reaction mixture (Hp-Na series).

# 3.2. Factors affecting the formations of mesophase and zeolite crystallization

The pH value and the amount of ethanol greatly affected the formation of mesophase as illustrated in Fig. 1 and in more detail in Fig. 2.



**Fig. 1.** Relationship between pH value and EtOH content with (Hp-Na(X)) and without (Hp-E(X)) the addition of NaOH under the presence of CTAB and TBAOH as the meso- and microtemplates, respectively.

Ethanol is miscible with water. When ethanol was added into the reactive solution, the solubility of surfactant CTAB would increase as the dielectric constant decreased in the whole solution. This change enhanced electrostatic repulsion among surfactant ions within micelles and weakened their hydrophobicity, which would lead to decreased stability of surfactant micelles and increased CMC value (critical micelle concentration) as well as decreased micellar size [22]. Specially, micelles could not form under an excessive amount of ethanol in the mixing solution (Hp-E(17)). A similar phenomenon was also found in the mesoporous zeolite synthesis by hydrothermal route [11].

Fig. 2a shows an apparently increased 2-theta value in SAXRD at the increased ethanol adding amount, implying that the micelle size and the corresponding mesopore size in the self-assembled products became smaller.

The effect of pH value on mesoporosity can be essentially attributed to the concentration of counter ions (OH<sup>-</sup>) to CTAB micelles. Counter ions, OH<sup>-</sup>, can compress the double-layer of micelles and also reduce electrostatic repulsion among those surfactant ions in a micelle by compensating the positive charges of CTAB when entering the core of CTAB micelles, which will enhance the stability of the CTAB micelles. Therefore, when NaOH was added into the reaction system, well ordered mesoporous structure can be achieved even at the highest content of ethanol (Fig. 2c, Hp-Na(17)) due to the enhanced stability of CTAB micelles. Apart from this, the ratio of  $V_{\text{micro}}/V_{\text{total}}$  (Table 1) was found decreased with the increasing amount of ethanol, which was similar to the literature report [11] and the authors contributed it to the hindering of ethanol to the crystallization of zeolite during hydrothermally treatment process. In our experiment, however, most of ethanol had been evaporated out before steam-treatment (crystallization), therefore, ethanol in fact played a different role in the formation of mesoporous zeolites in the present case. That the pore size became smaller at increased ethanol amount implys the number increases of the CTAB micelles and the corresponding mesopores under the same content of CTAB, leading to the increased mesopore volume and decreased ratio of  $V_{\text{micro}}/V_{\text{total}}$ , accordingly.

On the other hand, from Fig. 2a and b, one can know that a certain amount of ethanol addition do not affect the formation of mesophase but over high amount of ethanol would lead to the destruction of ordered mesophase, and meanwhile, even at very high pH value by NaOH addition, mesostructure can still be retained.

ZSM-5 zeolite usually form at high pH value (here, pH = 11.9), as reported in a large number of literatures [23,24]. At lower pH values, zeolite cannot be obtained, such as sample Hp-E(0) of pH = 10.7, which was found to be amorphous mesoporous silica with ordered pore structure (MCM-41). With the increase of pH value, crystallized zeolite phase gradually formed in products, such as Hp-E(4). In our experiments, the minimum pH value for the zeolite crystallization was found to be 10.80.

In an ethanol/water mixed solution under the presence of both micro- and mesotemplates (TBAOH and CTAB in the present case), pH value would increase significantly with the increase of ethanol amount and the addition of NaOH (Fig. 1), which affected the interactions among various species in the mixture and finally resulted in thoroughly different products.

### 3.3. Mesoporous zeolite formation as a result of adsorption competition and electrostatic interaction balances

#### 3.3.1. Adsorption competition balance for the co-existence of mesoand micro-colloids

Under the co-existence of CTAB and TBAOH templates, an adsorption competition balance to the inorganic species between CTAB and TBAOH must be achieved for the final formation of mesoporous zeolite, i.e., inorganic species should not be preferentially

Table 1
Textual properties of mesoporous zeolites synthesized in the shaded area in Fig. 1 <sup>a</sup> .

	$S_{\rm BET} (m^2  { m g}^{-1})$	$S_{\rm external/meso} ({ m m}^2{ m g}^{-1})$	$S_{ m micro}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\rm total}({ m cm}^3{ m g}^{-1})$	$V_{ m micro}~( m cm^3~g^{-1})$	Dv ( <i>d</i> ,nm)	$V_{\rm mic}/V_{\rm total}$	pH Value
Hp-E(10)	445	330	115	0.365	0.057	2.54	0.16	11.10
Hp-E(12)	364	198	166	0.200	0.086	2.35	0.43	11.25
Hp-E(13)	374	185	189	0.228	0.097	1.82	0.42	11.30
Hp-Na(0)	418	242	176	0.220	0.090	2.23	0.43	11.12
Hp-Na(4)	370	219	151	0.246	0.078	1.98	0.32	11.24
Hp-Na(7)	410	242	168	0.355	0.087	1.65	0.25	11.30

<sup>a</sup>  $S_{\text{BET}}$  (surface area) by BET method;  $S_{\text{micro}}$  (micropore surface areas) and  $S_{\text{external}}$  (external surface areas) and  $V_{\text{micro}}$  (micropore volumes) by *t*-plot method;  $V_{\text{total}}$  (total pore volumes of  $P/P_0 = 1$ ) was calculated by BJH method. Dv was the peak pore size according to pore size distribution. The pH value was measured in the reaction system.



Fig. 2. Small-angle XRD (a and c) and wide-angle XRD (b and d), patterns of Hp-E(X) (a and b), and Hp-Na(X) (c and d).

adsorbed to only one kind of templates (such as CTAB) but not to the other (such as TBAOH), or vice versa. This means that mesoand micro-colloids, formed by silicate species adsorbing onto mesotemplates (CTAB in the present study) and microtemplates (TBAOH) should be co-existent in the reaction systems. For example, according to Fig. 1, at relatively high pH value, i.e., at the increased [OH<sup>-</sup>], the double-layer of CTAB micelles was compressed and meanwhile, the stability and the charge density of the CTAB micelles were enhanced. Comparatively, the electric charging of TBAOH molecules was almost unchanged. Therefore, the inorganic species preferentially and mostly adsorb onto CTAB micelles when the pH value is excessively high, e.g., higher than 11.3 as illustrated in Scheme 1. As a result, only mesoporous structure without microporosity (or zeolite crystallization) can be generated. As a typical example, Hp-Na(10) was found to be amorphous mesoporous structure, because Hp-Na(10) had excessively high NaOH content. Therefore, it is very necessary to properly reduce pH value in primary reaction system. In our experiment, the maximum pH value for the successful formation of mesoporous zeolite was 11.30.

## 3.3.2. Balanced electrostatic interaction for the subsequent formation of mesoporous zeolite

As discussed above, in a slightly lowered pH value, inorganic species can be adsorbed on both meso- and microtemplates in comparable extents and an organic/inorganic composite colloidal solution can be obtained. Under this circumstance, keeping a balanced electrostatic interaction between meso-colloids and microcolloids should be a next essential key for binding the two kinds of colloids together for the formation of mesoporous zeolite phase without the phase separation between the mesoporous phase and zeolite crystal phase. Such an electrostatic interaction between two template colloids was also affected by pH value, i.e., by the surface charge densities of two kinds of composites. In this experiment, the pH values of all reactions solution are higher than 10.5, and in this



Scheme 1. The adsorption competition, electrostatic repulsion and mesoporous self-assembly from zeolites seeds under various pH values. SEM image is that of a typical product, sample Hp-E(7) showing the phase separation.

range, report [25] shows that the absolute zeta potential value of silicate species would decrease as pH value increases, implying the weakened electrostatic repulsion resulted from the surface charge between two kinds of composite colloids. When pH value was in a range of 10.8-11.1 in our experiment, the electrostatic repulsion between meso-colloid and micro-colloid is still high enough to compel each other resulting in phase separation (such as Hp-E(4) and Hp-E(7)). Once the pH value was higher than 11.1, as indicated in Fig. 1, the electrostatic interaction (as well as absolute zeta potential value) is inferred to have decreased substantially, leading to favorable affinity and/or integration between these two kinds of colloids for further free energy minimizing in the mixture. As a result, a mesoporous zeolite precursor without any phase separation was obtained during the following steam-assisted crystallization process. All above experimental and literature results means that there may exists a pH range where the inorganic species were adsorbed onto both meso- and microtemplates in a comparable way and the two kinds of composite colloids can be integrated together with each other under substantially minimized electrostatic repulsion, forming desired integral mesoporous zeolite phase, instead of amorphous mesoporous phase alone or phase-separated mesophase and zeolite crystals. In the present study, such a pH range was found be very narrowly in 11.10–11.30.

In summary, pH value is the most important key to the successful synthesis of mesoporous zeolite. Only in a very narrow pH range of 11.10–11.30, achieved by tuning the ethanol adding amount and/or

NaOH addition, mesoporous zeolite was found to be able to obtain. Higher or lower pH value would lead to either phase separation (a mixture of zeolite crystals and amorphous silica), or formation of amorphous phase alone, or even disordered amorphous silica, due to the preferential adsorption of inorganic species only onto one kind of templates and/or over high electrostatic repulsion between the composite colloids in solvent of high dielectric constant.

#### 4. Microstructure and catalytic properties

Sample Hp-Na(0) was used as an example for further characterizing its meso- and micro-structure and catalytic performance. This sample was chosen due to its typical meso-/microporous structure, as well as the fact that no previous investigation has been made on the catalytic property of synthesized mesoporous zeolite using CTAB as mesoporogen but without using ethanol [11,16].

Representative TEM images of a synthesized mesoporous zeolite, sample Hp-Na(0), are given in Fig. 3 to reveal the micro/ meso-structure. Fig. 4 is a corresponding SEM image.

A higher magnification image at the particle rim shown in Fig. 3b reveals the three-dimensional sponge or worm-like mesoporous structure of the synthesized mesoporous zeolite. The HR-TEM image (Fig. 3c) taken from the square area marked in Fig. 3b demonstrates clear single crystalline lattice fringes co-existing with the meso-structure, which is confirmed by the corresponding electron diffraction pattern. A d-placing of 0.98 nm measured from the HR-TEM images is in agreement with XRD results (at  $2\theta = 8.98^{\circ}$ , to (020) lattice plane). The co-existence of a meso-structure and zeolite lattice should be attributed to properly controlled pH value in the synthesis.

The mesoporous structure of Hp-Na(0) was measured by recording the nitrogen sorption isotherm (Fig. 5), which exhibits a typical type-IV behavior of mesoporous structure. A strong uptake of N<sub>2</sub> as a result of capillary condensation can be observed in a relative pressure ( $P/P_0$ ) range of 0.15–0.45 which indicates that the material has a typical mesoporous structure with mesopore size about 2.2 nm from the pore size distribution plot (inset in Fig. 5). A high Brunauer–Emmet–Teller (BET) surface area of 418 m<sup>2</sup> g<sup>-1</sup>, a total pore volume of 0.22 cm<sup>3</sup> g<sup>-1</sup>, and the corresponding microporous volume, the meso- and micropore surface areas can be found in Table 1.

The catalytic application of synthesized mesoporous zeolite in biodiesel fabrication was explored (see Scheme 2). Fig. 6 shows the yield vs. time plots of ethyl laurate, in which Hp-Na(0) demonstrates distinctively higher activity than those of ZSM-5, Al-MCM-41 in the first 8 h. Typically the yield of ethyl laurate when using Hp-Na(0) as the catalyst is about 2.3 and 3.4 times of those using ZSM-5 and Al-MCM-41 as catalysts in 16 h of reactions under the same condition. This result confirmed that the reaction was controlled both by a diffusion step in the pore network and by an acid catalytic step. The diffusion limitation in the micropore channel of ZSM-5 or the weak acidity in the mesoporous Al-MCM-41 have led to significantly lower catalytic efficiencies in this reaction. In the other word, the extensive mesoporosity and the high acidic intensity of Hp-Na(0) ensures its high production yield of ethyl laurate due to its much more efficient diffusion of large molecule reac-



Fig. 3. (a) TEM image of a representative particle of Hp-Na(0), (b) high magnification image at its rim, (c) HR-TEM image taken from the square frame in (b) and the inset is the corresponding electron diffraction pattern.



Fig. 4. Representative SEM image of hierarchical zeolite, sample Hp-Na(0).



Fig. 5.  $N_2$  sorption isotherms and the corresponding pore size distribution (inset) of sample Hp-Na(0).



Scheme 2. Esterification of lauric acid with ethanol to produce ethyl laurate.

tants/products in mesopore channels of Hp-Na(0) than in the micropore network of ZSM-5 than that of Al-MCM-41 and higher catalytic activity than amorphous Al-MCM-41, respectively.

#### 5. Conclusion

In summary, a very narrow pH range of 11.10–11.30 has been found suitable for the successful synthesis of mesoporous zeolite in an ordinary two-step approach of zeolite seed formation-steam assisted crystallization using conventional surfactants CTAB and TBAOH as meso- and microtemplates, respectively. The pH value can be tuned either by changing the ethanol adding amount and/ or NaOH addition. Higher or lower pH value would lead to either phase separation (a mixture of zeolite crystals and amorphous silica), or formation of amorphous phase alone, or even disordered amorphous silica, due to the preferential adsorption of inorganic species only onto one kind of templates, or the over high electro-



Fig. 6. Ethyl laurate yield in the esterification of lauric acid with ethanol using different kinds of catalysts.

static repulsion between the composite meso- and micro-colloids. The obtained mesoporous zeolite showed greately enhanced catalytic activity in the esterification of lauric acid with ethanol for ethyl laurate production.

#### Acknowledgements

The authors thank the financial support from National Natural Science Foundation of China (No. 20633090 and 20703055), Natural science fund for colleges and universities in Jiangsu Province (No. 09KJD430010) and in Fujian Province of China (No. JB10131) and also thanks the Priority Academic Program Development of Jiangsu Higher Education Institutions.

#### Reference

- [1] C.L. Li, Y.Q. Wang, B.F. Shi, J.W. Ren, X.H. Liu, Y.G. Wang, Y. Guo, Y.L. Guo, G.Z. Lu, Microporous Mesoporous Mater. 117 (2009) 104–110.
- [2] C.S. Cundy, P.A. Cox, Chem. Rev. 103 (2003) 663-701.
- [3] G. Caeiro, R.H. Carvalho, X. Wang, M.A.N.D.A. Lemos, F. Lemos, M. Guisnet, F. Ramoa Ribeiro, J. Mol. Catal., A: Chem. 255 (2006) 131–158.
- [4] A. Corma, Chem. Rev. 97 (1997) 2319-2373.
- [5] J. Perez-Ramirez, S. Abello, L.A. Villaescusa, A. Bonilla, Angew. Chem., Int. Ed. 47 (2008) 7913–7917.
- [6] C.S. Mei, Z.C. Liu, P.Y. Wen, Z.K. Xie, W.M. Hua, Z. Gao, J. Mater. Chem. 18 (2008) 3496–3500.
- [7] J. Zhou, Z.L. Hua, J.L. Shi, Q.J. He, L.M. Guo, M.L. Ruan, Chem. Eur. J. 15 (2009) 12949–12954.
- [8] J. Zhou, Z.L. Hua, J.J. Zhao, Z. Gao, S.Z. Zeng, J.L. Shi, J. Mater. Chem. 20 (2010) 6764–6771.
- [9] J.J. Zhao, Z.L. Hua, Z.C. Liu, Y.S. Li, L.M. Guo, W.B. Bu, X.Z. Cui, M.L. Ruan, H.R. Chen, J.L. Shi, Chem. Commun. (2009) 7578–7580.
- [10] H. Wang, T.J. Pinnavaia, Angew. Chem., Int. Ed. 45 (2006) 7603-7606.
- [11] Y. Zhu, Z.L. Hua, J. Zhou, L.J. Wang, J.J. Zhao, Y. Gong, W. Wu, M.L. Ruan, J.L. Shi, Chem. Eur. J. 17 (2011) 14618–14627.
- [12] F.S. Xiao, L.F. Wang, C.F. Yin, K.F. Lin, Y. Di, J.X. Li, R.R. Xu, D.S. Su, R. Schlogl, T. Yokoi, T. Tatsumi, R. Schlogl, T. Yokoi, T. Tatsumi, Angew. Chem., Int. Ed. 45 (2006) 3090–3093.
- [13] M. Chio, H.S. Cho, R. Srivastava, C. Venkatesan, D.H. Choi, R. Ryoo, Nat. Mater. 5 (2006) 718-723.
- [14] M. Chio, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, Nature 461 (2009) 246–250.
- [15] Y.D. Xia, R. Mokaya, J. Mater. Chem. 14 (2004) 863-870.
- [16] H. Li, J.J. Jin, W. Wu, C.C. Chen, L. Li, Y.S. Li, W.R. Zhao, J.L. Gu, G.R. Chen, J.L. Shi, J. Mater. Chem. 21 (2011) 19395–19401.
- [17] J. Cejka, S. Mintova, Catal. Rev.-Sci. Eng. 49 (2007) 457–509.
  - [18] J. Perez-Ramirez, C.H. Christensen, K. Egeblad, C.H. Christensen, J.C. Groen, Chem. Soc. Rev. 37 (2008) 2530–2542.
  - [19] X.J. Meng, F. Nawaz, F.S. Xiao, Nano Today 4 (2009) 292-301.
  - [20] M. Haouas, D.P. Petry, S.C.C. Wong, A. Aerts, C.E.A. Kirschhock, J.A. Martens, S.J. Gaskell, M.W. Anderson, F. Taulelle, J. Phys. Chem. C 113 (2009) 20827–20836.
  - [21] S. Bals, K.J. Batenburg, D. Liang, O. Lebedev, G. Van Tendeloo, A. Aerts, J.A. Martens, C.E.A. Kischhock, J. Am. Chem. Soc. 131 (2009) 4769–4773.

- [22] Z. Zheng, Physical Chemistry of Surfactants Principle, South China University of Technology Press, 1997 (in Chinese).
  [23] A.A. Ismail, R.M. Mohamed, O.A. Fouad, I.A. Ibrahim, Cryst. Res. Technol. 41 (2) (2006) 145–149.
- [24] A. Sarioglan, O.T. Savasci, A. Erdem-Senatalar, A. Tuel, G. Sapaly, Y.B. Taarit, J. Catal. 246 (2007) 35–39.
   [25] Y. Xin, Pant & Coatings Industry, 36(8) (2006), 58–60 (in Chinese).