

FABRICATION OF MESOPOROUS WITHIN ZEOLITE Y USING MIXED TEMPLATES

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Mesoporous zeolite Y was prepared using a block copolymer and hexadecyltrimethyl ammonium bromide as mixed templates. Copolymer-ionic surfactant complexes were formed and grafted into aluminosilicate gel, introducing mesoporous into zeolite. The XRD results indicated the mesoporous sample showed high crystalline and hydrothermal stability indicating a negligible damaging effect on the framework. Nitrogen adsorption and desorption results of mesoporous zeolite showed the uniform property of mesopore size distribution in the range of 2.0-5.0 nm with a greater surface area ($630 \text{ m}^2\text{g}^{-1}$), mesopore volume ($0.324 \text{ cm}^3 \text{ g}^{-1}$), and mesopore area ($99 \text{ m}^2\text{g}^{-1}$). A novel method was provided to develop an available mesoporosity.

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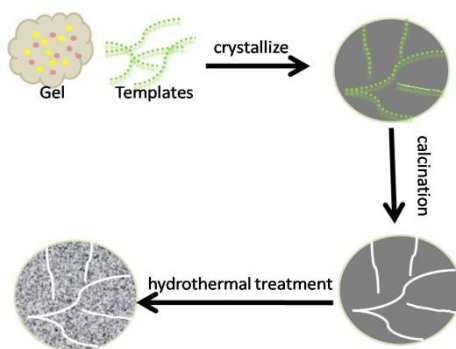
1. Introduction

Zeolite Y is of primary importance in petrochemical processes and refining, owing to their ordered micropores [1]. The unique micropores structure creates a large specific surface area and high acidity, as well as the good shape selectivity [2]. And the diffusional limitations are usually observed of bulky reactants/products in/out of the zeolite. To overcome such a problem, mesoporous zeolites with large pores are produced.

To synthesize mesoporous zeolite, a considerable number of approaches have been reported in the previous documents. One is the top-down approach with no templates. In this method, mesoporous zeolites are obtained through dealumination or desilication treatment in acid or alkaline etching [3]. Unfortunately, defect of crystalline framework is inevitably introduced in this process [4]. Meanwhile, alkaline treatment only is suit for zeolites with a native Si/Al ratio in the 25–50 range [5]. As the process of demetallization of Al or Si is not easy to control, the distribution of the introduced mesoporous is not uniform and the connectivity is poor [6]. Correspondingly, another strategy is bottom-up approach with templates. Based on the published reviews in recent years, templates are typically divided into two categories: hard template and soft template. Hard template methods are performed by introducing solid materials into the gel precursor to act as mesoporous templates in the crystallization process [7]. Carbonaceous templates are the most investigated type of hard templates [8-10]. However, Due to the hydrophobicity of solid materials, combining force between the templates and mother gel is weak, and phase separation occurs easily during the crystallization process. These drawbacks limit the applications of hard templates. Besides hard templates, soft templates also are used as another effective template to introduce porosity into zeolite material. Surfactants and polymers are the

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most common ones [7,11]. Block copolymers are highly commercialized products and now widely used for the directly synthesis of mesoporous materials owing to its excellent aggregation property. According previous researches, block copolymers have been employed to get hierarchically porous zeolites [12,13]. Recently, it was reported that copolymer can bind cooperatively with ionic surfactants micelles [14]. And copolymer–ionic surfactant complexes can be also formed and template the formation of mesopores [15]. In the previous work, mesoporous zeolites containing mesoporosity were successfully synthesized with the template of F127 [16]. In this paper, high utilization rate of raw materials was achieved from zeolite precursor gel with low Si/Al compared to previous research. Base on this green synthesis, a further research was carried out to produce mesopores using copolymer–ionic surfactant complexes (pluronic F127 and hexadecyltrimethyl ammonium bromide CTAB) as mixed templates. The formation mechanism of mesoporous zeolites Y using mixed-templating synthesis strategy was shown in Schematic 1. Mesoporous zeolites Y were obtained with high crystalline and uniform mesopore property.



Schematic 1. The formation mechanism of mesoporous zeolites Y using mixed-templating synthesis strategy.

2. Experimental

Zeolite Y was prepared as described previously [16]. The mesoporous zeolite Y was prepared from a precursor gel with the following molar composition: (2.0–2.5) Na₂O:Al₂O₃:7.5 SiO₂:150 H₂O: 0.003 CTAB: 0.0005 F127. After being stirred for 2 h, the mixture was transferred to a stainless steel autoclave and hydrothermally treated at 98 °C for 16 h. After filtration, dried, and calcinated in air at 550 °C for 6 h to remove the templates, the final product was denoted as MZY. For comparison, zeolite Y was obtained using the same process without addition of mixed templates, and named as ZY.

The ultra-stable zeolites Y were prepared by ions exchanged with 1.0 M (NH₄)₂SO₄ solution. After hydrothermal treatment at 600 °C for 2 h, the samples were denoted as MUSY and USY respectively.

X-ray diffraction (XRD) patterns of the prepared zeolites were recorded on a Bruker AXSD8 Advance using nickel-filtered Cu K α X-ray radiation at 40 kV and 30 mA. The crystallinity of the zeolites was estimated from the reflections of the (hkl) values of (311), (333), (440), (533), (642), (660), (555) and (664). The summation of the areas under these peaks was used to quantify the relative crystallinity. The crystallinity of zeolite Y (ZY) was taken as 100%. The specific surface areas and pore volumes of the zeolites were measured using a Bilder MD-200 system. The total specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. The total pore volumes were calculated from the amounts of nitrogen adsorbed at P/P₀ = 0.98. The micropore volumes were calculated by the t-plot method. Barrett–Joyner–Halenda (BJH) model was used to obtain pore size distribution from the adsorption. Scanning electron microscopy (SEM) was used to describe the morphology of the samples on a Quanta 200 (FEI Co., Netherlands) apparatus. Transmission electron microscope (TEM) was obtained using a JEOL JEM-2100 electron microscope operating at 200 kV.

3. Results and discussion

As shown in Fig. 1, XRD patterns of the zeolites Y (ZY, MZY) and ultra-stable zeolites Y (USY, MUSY) showed the typical diffraction peaks for a FAU type zeolite. Compared with ZY, MZY sample had a high crystallinity indicating that the addition of templates had a negligible damaging effect on the framework of the zeolite. Ultra-stable zeolites Y appeared a low crystallinity referring to zeolites Y. It is attributed to the defects introduced by hydrothermal treatment [17]. The drop of crystallinity of MZY samples (2%) was lower than that of ZY (6%), revealing that the mesoporous products had high hydrothermal stability.

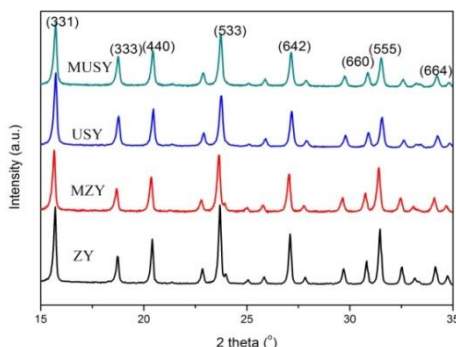


Fig. 1. XRD patterns of zeolites.

Fig. 2 illustrated the nitrogen adsorption-desorption isotherms of the samples. Nitrogen sorption isotherm of parent ZY showed an isotherm Type I and no hysteresis loop revealing the presence of only micropores in the structure. Both MZY and MUSY samples obtained from the mixed template exhibited Type IV isotherms with H-IV hysteresis loops. The sharp nitrogen adsorption was seen in high relative pressures (>0.5) attributed to the introduction of mesopores [18]. BJH pore size distribution curves (Fig. 3) presented their diameters were obviously centralized in the range of 2–5 nm. However, it was not occurred about the sample USY. It was revealing that the mesopores produced by mixed templates presented a concentrated distribution comparing to mesoporous created in hydrothermal process. These results indicated that mixed templates supported the formation of uniform mesophase. The analysis of the pore structure is listed in Table 1. Referring to ZY, the MZY sample exhibited a greater surface area ($630 \text{ m}^2 \text{ g}^{-1}$), mesopore volume ($0.324 \text{ cm}^3 \text{ g}^{-1}$), and mesopore area ($99 \text{ m}^2 \text{ g}^{-1}$), attributing to the presence of obvious mesoporous structures. After hydrothermal treatment, the resultant sample USY showed a more decrease of micropore area and volume than that of mesoporous sample MUSY. It indicated that the less decrease of microporosity caused by destruction of zeolite framework [19]. These results indicated that a higher hydrothermal stability of MZY than ZY. Therefore, mixed template is a good method to introduce mesoporosity with high crystalline.

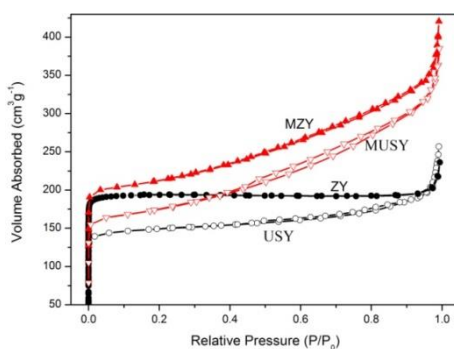


Fig. 2. Nitrogen adsorption-desorption isotherms of zeolites.

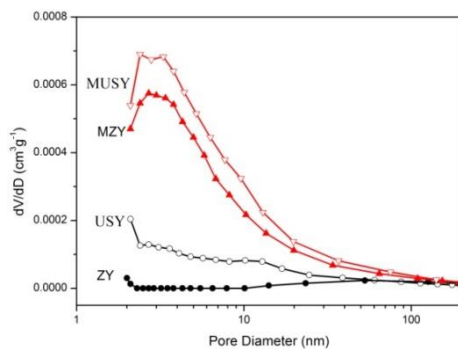


Fig.3. BJH pores size distribution of zeolites.

The crystallite size and morphology of the zeolite samples were investigated by SEM (Fig. 4a-d). The SEM images of samples MZY (Fig.4b) and MUSY (Fig.4d) showed the typical octahedral morphology consisting particle of size in the range of 600-800nm, which was similar to ZY (Fig. 4a) and USY (Fig. 4c).

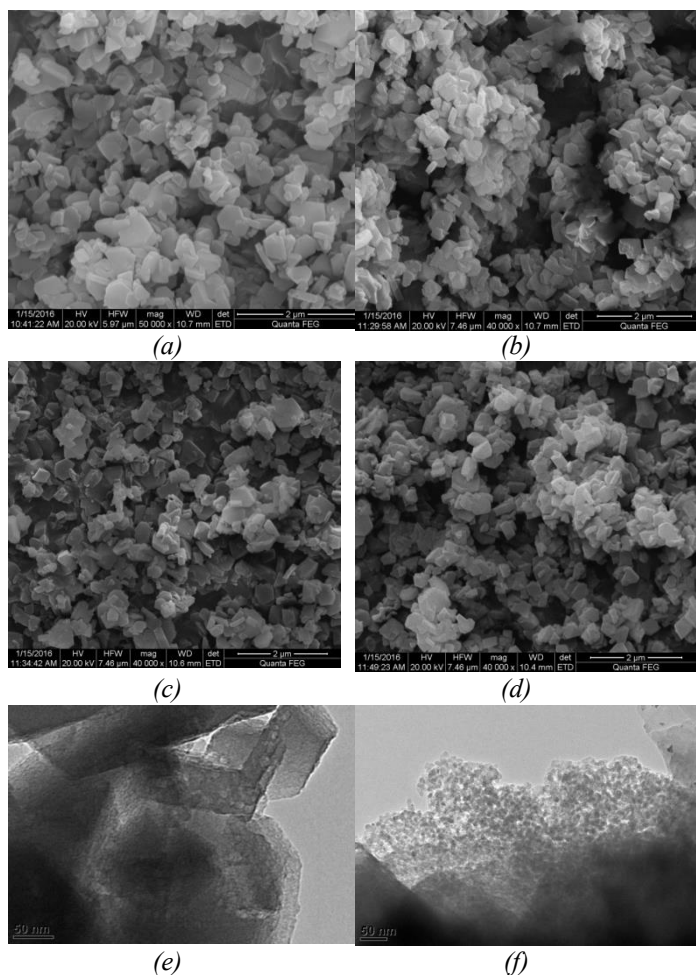


Fig. 4. Electron microscopes of samples: (a and b) SEM images of ZY and MZY, (c and d) SEM images of USY and MUSY, (e and f) TEM images of USY and MUSY.

In addition, few amorphous material was observed in the mesoporous zeolites MZY and

MUSY. These results indicated that the addition of mixed templates into the gel did not affect the synthesis of zeolite with high crystallinity. Furthermore, the intracrystalline mesopores inside the crystals can be observed evidently (Fig. 4e-f). The TEM images of MUSY (Fig.4f) showed that the single crystal exhibited more bright spots comparing to common USY. These bright spots were attributed to the presence of mesopores, which were likely to penetrate into crystals. The TEM images prove that the mixed templates took a significant effect on creating mesoporous systems within zeolite crystal.

Table 1. Textural parameters of zeolites.

| Samples | Surface area ($\text{m}^2 \text{g}^{-1}$) | | | Pore volume ($\text{cm}^3 \text{g}^{-1}$) | | | Relative crystallinity |
|---------|---|------------------|-------------------|---|------------------|-------------------|------------------------|
| | S_{total} | S_{mic} | S_{meso} | V_{total} | V_{mic} | V_{meso} | |
| ZY | 562 | 551 | 11 | 0.365 | 0.299 | 0.066 | 100% |
| USY | 455 | 399 | 56 | 0.397 | 0.230 | 0.167 | 94% |
| MZY | 630 | 531 | 99 | 0.651 | 0.327 | 0.324 | 98% |
| MUSY | 551 | 439 | 111 | 0.576 | 0.269 | 0.327 | 96% |

4. Conclusions

We have synthesized mesoporous zeolite Y using pluronic F127 and hexadecyltrimethyl ammonium bromide as mixed templates. After being hydrothermal treatment, mesoporous USY exhibited uniform textural properties and the intracrystalline mesopores about 2-5 nm exist inside the crystal. The mesoporous zeolite presented well preserving crystallinity and high hydrothermal stability. This new method developed using mixed templates not only can be used to directly prepare mesoporous zeolite Y, also other mesoporous materials applied widely in oil refining.

Acknowledgments

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