Synthesis of Mesoporous ZSM-5 Zeolite and Its Adsorption Properties for VOCs

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Abstract. A composite template method was used to synthesize a ZSM-5 molecular sieve containing intracrystalline mesopores. In this paper, the charge ratio and the amount of mesoporous template have been set as variables. The synthesized samples were characterized through XRD, TEM and BET and its absorption performance of toluene has been qualitatively analyzed. The results showed that the synthesis of ZSM-5 structure required a suitable charge ratio and the amount of composite templating agent. The specific surface area of molecular sieve with ZSM-5 structure can be up to 499 m²/g, which charge ratio was 0.8. Besides, the maximum of adsorption amount of static adsorption and adsorption rate of dynamic adsorption were 265 mg/g and 16.75% respectively.

1. Introduction
ZSM-5 zeolite molecular sieve is a crystalline aluminosilicate porous material, has the advantages of high acid resistance, thermal stability, hydrophobicity, non-flammability, etc.[1]. The traditional ZSM-5 zeolite is a microporous pore structure, which restricts the adsorption ability of macromolecular substances as an adsorbent. And the pores of the zeolite could be easily blocked and deactivated in a short time. Therefore, the application of adsorbing macromolecular volatile organic compounds (VOCs) had been greatly limited. There are increasing problems caused by VOCs, mainly due to the harmful effects of some components on the environment and the health. Therefore, it is necessary to explore suitable treatments of VOCs. In previous studies, it was found that to introduce mesopores to the
microporous pore structure, these ZSM-5 zeolite molecular sieves can absorb organic macromolecules as well.

At the beginning, the ZSM-5 molecular sieve was synthesized by using tetrapropylammonium hydroxide which contains quaternary ammonium salt cation as the soft template[2]. Templats such as n-propylamine, hexamethyleneimine, tetrapropylammonium and their composites could be used for synthesizing different sizes of ZSM-5 molecular sieves[3]. Lee et al.[4] synthesized a ZSM-5 molecular sieve that did not require removal of the templating agent by calcination. ZSM-5 zeolite with regulated pore and pore structure was synthesized by using 10 nm carbon particles as hard template, but the distribution of micropores and mesopores was uneven[5]. In previous studies, nanocrystalline ZSM-5 with mesoporosity was synthesized within a short reaction time using triethoxyphenylsilane as the mesopore structure[6].

In this paper, ZSM-5 molecular sieves containing intracrystalline mesopores were synthesized by the composite templating agent through soft template method. The effects of the charge ratio of anionic surfactants and cationic polymers on the structural properties of molecular sieves were also investigated. Toluene was used to characterize the adsorption performance of intramolecular mesoporous ZSM-5.

2. Experiment

2.1. Preparation of molecular sieves

Mesoporous ZSM-5 was synthesized by using cationic polymer and anionic surfactant as composie templating agent. A monomer molecule of cationic polymer carries a positive charge and a monomer molecule of anionic surfactant carries a negative charge. Therefore, the charge ratio of the anionic surfactant and the cationic polymer is equal to the molar ratio of the two. The previous study illustrated that the charge ratio can be changed by changing the adding amount of composite templates. Hence, a series of samples with different charge ratio (X stood for charge ratio, X=0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) have been set and numbered as D-ZSM-5-X. The molar ratio of raw material is 1 SiO$_2$: a Al$_2$O$_3$: b TPAOH: c NaOH: d H$_2$O: x anionic surfactant: e cationic polymer, wherein a, b, c, d, e were fixed numerical ratio while x=0.0125, 0.025, 0.05, 0.075, 0.1, 0.125, x: e= X. And the samples were prepared through hydrothermal reaction.

2.2. Catalyst characterization

X-ray diffraction analysis is the XRD test. The instrument used in this analysis method was a Bruker D8 Advance X-ray diffractometer manufactured by Bruker, Germany. The test conditions was setting under step scan mode with 0.02° per step, scan rate 2°/min, scan range 2θ=5~90°.

Transmission Electron Microscope (TEM) analysis has used a TEM analyzer model JEM-2100F manufactured by JEOL. The transmission diagram of the sample can be obtained by HRTEM test analysis. The microscopic appearance and shape profile of the sample and its mesoporous shape distribution can be showed. Test conditions was that sample dispersion (ethanol, ultrasound).

BET test analyzer was the Micromeritics ASAP-2020 adsorption analyzer produced by American Micron Company. The partial pore size parameter such as specific surface area (S$_{BET}$), outer surface area (S$_{EXT}$), total pore volume (V$_p$), micropore pore volume (V$_{micro}$), mesoporous pore volume (V$_{meso}$), and average pore size (D$_{aver}$) can be obtained. The experiment was divided into two stages, pretreatment and analysis. Pretreatment conditions was to degas at 180°C for 6h.

2.3. Catalyst performance evaluation

Due to the complex and diverse composition of VOCs and the limitations of laboratory conditions, toluene, was selected as one of the most common VOCs.

The instrument used in the static adsorption experiment was the fully automatic intelligent weight adsorption instrument IGA-002 (briefly called as IGA) produced by Hiden, UK. with the theory of gravimetric method. It automatically recorded the static adsorbance of the sample and various variation parameters during the experiment. The parameters we need are the relationship between the weight and
3. Results and discussion

3.1. Characterization results of mesoporous ZSM-5 molecular sieves

3.1.1. XRD analysis. XRD characterization experiments were carried out on ZSM-5 molecular sieve samples synthesized under different charge ratio conditions to qualitatively analyze the structure and crystallinity of the synthesized molecular sieve samples. The results of the XRD experiment were shown in Figure 1.

When the charge ratio of the anionic surfactant and the cationic polymer was 0.1, the XRD pattern of the sample did not show any diffraction peak, and the sample exhibited an amorphous structure. It indicated that when the charge ratio was too small, there were competing effect between the excessive cationic polymer and the TPA$^+$ ions, which lead to the synthesized sample being an amorphous aluminosilicate material. When the charge ratio increased to 0.2, it can be seen from the XRD pattern that the D-ZSM-5-0.2 sample exhibited a diffraction peak characteristic of the ZSM-5 zeolite molecular sieve. It indicated that with the addition of anionic surfactant, good compatibility between the zeolite precursor formed by the silica species in the slurry and the excess cationic polymer has shown, which was beneficial to the bonding assembly of the zeolite precursor. As the charge ratio increased, that is, the addition amount of anionic surfactant increased, the XRD pattern diffraction peak intensity of D-ZSM-5-0.4 and D-ZSM-5-0.6 enhanced, which indicated that the synthesized sample has better crystallinity. When the charge ratio increased to 0.8, the intensity of the XRD pattern diffraction peak of the synthetic sample D-ZSM-5-0.8 decreased, because the competition effect between mesoporous templating agent and silicon-aluminum species was too strong to affect the crystallinity of synthetic samples. It was found that when the charge ratio beyond 0.8, a relatively viscous white gelatinous substance appeared and a small amount of precipitation occurred during the preparation of the sample. When the charge ratio reaches 1.0, the XRD pattern of the synthetic sample D-ZSM-5-1.0 did not show the diffraction peak of ZSM-5 molecular sieve but the formation of the amorphous structure of the species. It can be known that when the charge ratio was too high that restrained the TPAOH to induce the formation of MFI structure. At the same time due to too much mesoporous templating agent, the silicon-aluminum species would strongly combine with it, resulting in insufficient reaction solution around the microporous template and difficulties in crystallization and nucleation.

![Figure 1. XRD pattern of ZSM-5 molecular sieve synthesized under different conditions.](image-url)
3.1.2. Specific surface and pore analysis. Through the use of the experimental data measured by the fully automatic surface area and microporous pore analysis instrument, after a series of drawing and comprehensive sorting, the results were shown in Figure 1, Figure 2 and Table 1.

It can be seen from Figure 2 that the N$_2$ adsorption-desorption isotherm was determined in a liquid nitrogen environment to characterize the specific surface area, pore volume and pore structure of the ZSM-5 molecular sieves with different charge ratios synthesized by the soft template method. Their adsorption isotherm curve are conformed to the characteristics of the IV isotherm. When the pressure P/P$_0$=0.4, the isotherm showed an upward trend. And the adsorption isotherm and the desorption isotherm did not coincide, forming a closed loop. This was due to the presence of mesopores in the synthesized ZSM-5 molecular sieve, which caused a capillary condensation during the BET experiment, and formed a hysteresis loop unique to the mesoporous material in the N$_2$ adsorption and desorption experiment.

As it can be seen from Figure 3, there were subtle differences in the mesoporous pore size distribution of the six ZSM-5 molecular sieve samples with different charge-synthesized. When the charge ratio is 0.1, the proportion of mesopores distributed between 2 and 15 nm; when the charge ratio is 0.2 and 0.4, the pore size was mostly 2~20nm; when the charge ratio increased to 0.6 and 0.8, the pore size distribution range of mesopores expanded to 2~35nm; when the charge ratio is 1.0, the mesoporous pore size distribution concentrated in 2~20 nm. But the MFI structure had not been found in D-ZSM-5-0.1 and D-ZSM-5-1.0 as the reasons had been illustrated through XRD analysis.

![Figure 2](image1.png)

**Figure 2.** N$_2$ adsorption and desorption curve of ZSM-5 molecular sieve synthesized under different conditions.

![Figure 3](image2.png)

**Figure 3.** Mesoporous distribution of nanocrystalline ZSM-5 zeolite synthesized under different conditions.
Despite of D-ZSM-5-0.1 and D-ZSM-5-1.0 which were amorphous structures, the trend of the specific surface area and the pore parameter of the other four samples were shown in Table 1. When the charge ratio was 0.2, the specific surface area is 345 m$^2$/g. When the charge ratio increased, the specific surface area increased as well. And when the charge ratio was 0.6, its specific surface area peaked at 499 m$^2$/g then decreased as charge ratio increased. The external surface area also increased from 282 m$^2$/g of sample D-ZSM-5-0.2 to 435 m$^2$/g of sample D-ZSM-5-0.6. Its total pore volume $V_p$ and its pore volume $V_{meso}$ were also similar to the trend of specific surface area and external surface area. It showed a peak at a charge ratio of 0.6 and decreased as the charge ratio exceeded 0.8; its pore volume did not change much. The amplitudes are all in the range of 0.02–0.04cm$^3$/g. The average pore diameter $D_{aver}$ of the synthesized ZSM-5 molecular sieves tended to increase as the charge ratio increased.

### Table 1. Pore parameters of D-ZSM-5-X samples synthesized with different charge ratios.

|                | $S_{BET}$ (m$^2$/g) | $S_{EXT}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $V_{micro}$ (cm$^3$/g) | $V_{meso}$ (cm$^3$/g) | $D_{aver}$ (nm) |
|----------------|---------------------|---------------------|-------------------|-------------------------|------------------------|-----------------|
| D-ZSM-5-0.1    | 355                 | 264                 | 0.41              | 0.04                    | 0.45                   | 7.50            |
| D-ZSM-5-0.2    | 345                 | 282                 | 0.49              | 0.03                    | 0.55                   | 8.52            |
| D-ZSM-5-0.4    | 364                 | 280                 | 0.51              | 0.04                    | 0.54                   | 8.21            |
| D-ZSM-5-0.6    | 499                 | 435                 | 0.96              | 0.02                    | 1.04                   | 10.22           |
| D-ZSM-5-0.8    | 488                 | 413                 | 0.95              | 0.03                    | 1.02                   | 10.60           |
| D-ZSM-5-1.0    | 467                 | 399                 | 0.85              | 0.03                    | 1.08                   | 11.46           |

3.1.3. Microstructure analysis. Three samples with different charge ratios were selected for transmission electron microscopy (TEM). The three different charge ratios were 0.1, 0.4 and 0.8 respectively. The transmission electron micrograph of the sample D-ZSM-5-0.1 was shown in Figure 4a, 4b. It can be seen from the pictures that its morphology was irregular amorphous grain, but the particles had a small portion of intracrystalline mesopores. The transmission electron microscopy and electron diffraction of the sample D-ZSM-5-0.4 are shown in Figure 4c, 4d. Its shape was circular and there were many intragranular mesopores in the crystal grain. The transmission electron microscopy and electron diffraction of the sample D-ZSM-5-0.8 were shown in Figure 4e, 4f. The morphology of D-ZSM-5-0.8 was a uniform spherical shape and there were many intracrystalline mesopores in the crystal grains with the unsmooth edge of the contour. The sample had a high degree of crystallinity and its electron diffraction image also showed the presence of mesopores.

Figure 4. Transmission electron microscope and electron diffraction pattern of nanocrystalline ZSM-5 zeolite.

a & b: D-ZSM-5-0.1, c & d: D-ZSM-5-0.4, e & f: D-ZSM-5-0.8.
3.2. Evaluation of Adsorption Properties of Mesoporous ZSM-5 Molecular Sieves

The static toluene adsorption isotherms of ZSM-5 molecular sieves synthesized with different charge ratios were shown in Figure 5. Although sample D-ZSM-5-0.1 did not form the grain structure of ZSM-5, but its adsorption amount of toluene was the highest, which reached 312 mg/g. When the charge ratio is 1.0, the sample does not form the crystalline structure of ZSM-5 but its static adsorption amount of toluene can also reach 299 mg/g. When the charge ratios were 0.2, 0.4, 0.6 and 0.8, their static adsorption amount of toluene were 202 mg/g, 214 mg/g and 227 mg/g respectively, which showed a gradually increasing trend, indicating that the adsorption performance of ZSM-5 zeolite molecular sieve synthesized by soft template method increased with the increase of charge ratios.

It can be seen from the figure that the static adsorption of toluene by the ZSM-5 zeolite molecular sieve synthesized by the soft template method was close to the IV curve, and the adsorption amount of toluene reached about 200-310 mg/g. There were richer pore structure and higher mesoporous ratio in ZSM-5 molecular sieve synthesized by soft template method and its specific surface area and pore volume were more controllable. The formation of intramolecular mesopores was a macromolecular substance for adsorbing toluene. A greater interaction force would result in better adsorption.

Figure 5. Adsorption performance of ZSM-5 molecular sieves synthesized with different charge ratios on toluene

4. Conclusion

Mesoporous ZSM-5 zeolite molecular sieves were synthesized by soft template method. There were certain influences of the conditions of changing the charge ratio with different addition amount of mesoporous template on the crystallinity and pore structure of the synthesized samples. And the suitable charge ratio can even increase the specific surface area for about 154 m$^2$/g and the external surface area for about 153 m$^2$/g. The adsorption performance of toluene showed that the new ZSM-5 molecular sieve with crystal mesopores synthesized by soft template method can greatly increase the adsorption amount of toluene, which reached 200–310 mg/g during the static adsorption. And with larger mesoporous ratio, there were stronger interaction among the adsorbed molecules in the intracellular mesoporous adsorption process and better adsorption capacity were found. Therefore, it has a prospect that to enhance the adsorption of VOCs macromolecular substances by optimizing the structure and adsorption performance of mesoporous ZSM-5.

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