

Preparation and Characterization of SSZ-13 Molecular Sieve

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Abstract

SSZ-13 molecular sieve is prepared by the traditional hydrothermal method with silica sol, aluminium sulphate, sodium hydroxide and deionized water as raw material, and N, N, N-trimethyl-l-adamant ammonium hydroxide as a template. It is investigated in terms of the influencing factors and optimal reaction conditions, and characterized with XRD, BET specific surface area meter and FT-IR. The experimental results indicate that the obtained SSZ-13 molecular sieve has advantages of shorter reaction time, higher crystallinity and larger specific surface area. The reaction time is further shortened to 2 days by introducing crystal seed or accelerant, which lowers the total preparation cost of SSZ-13 and makes its industrialization highly feasible.

Keywords: SSZ-13 molecular sieve, N, N, N-trimethyl-l-adamant ammonium hydroxide, Accelerant

Preface

New types of zeolites have been continuously developed since the first artificial zeolite was successfully synthesized in 1948. They have been widely applied in such fields as petrochemical industry, metallurgy industry, metal processing, machine building, pesticide industry and environmental protection, and played an irreplaceable role in the industry and agriculture. Stacey I Zones (1985, US 4544538), an American chemist, prepared a new SSZ-13 molecular sieve by hydrothermal method in the 80s of 20th century. What he got is a chabazite (CHA), whose structure consists of a 3-D elliptic network of orderly arranged eight-membered rings with strictly alternating AlO₄ tetrahedron and SiO₄ tetrahedron being interconnected by oxygen bridges (Luis J S *et al*, 1997, p. 143-146). The channel size of SSZ-13 is 0.3 nm (Song *et al*, 2005, p. 807-812), and its specific surface area is up to 700 m²/g. It is classified as a member of micropore zeolites according to the channel size (Jeo H Y *et al*, 2006, p. 70-78). SSZ-13 may be used as a carrier for adsorbent (air-purifying agent, for example) or catalyst (automobile exhaust catalyst, for example) due to the excellent thermal stability resulted from its large specific surface area and distinctive eight-membered ring structure (Alexis M W *et al*, 2008, p. 193-199). The presence of AlO₄ and SiO₄ tetrahedrons in the framework results in the properties of cation exchange and acidity adjustability (Laura Regli *et al*, 2007, p. 12131-12140), which in turn makes SSZ-13 exhibit a good catalytic behaviour (Zhu Q J *et al*, 2007, p. 5409-5415). Therefore, SSZ-13 has been applied in the catalytic cracking of hydrocarbon compounds, as well as the constitution reaction of olefins and aromatics.

In addition, SSZ-13 works well in the methanol-to-olefin (MTO) catalysis (Zhu Q J *et al*, 2007, p. 5409-5415), and can increase the yield of low carbon olefin. However, it hasn't been reported so far in China as to this type of SSZ-13 molecular sieve because the template for it is very difficult to obtain and expensive, and its reaction period is too long (about 7 days), which leads to the increase of the cost of SSZ-13 molecular sieve. Therefore, it is necessary to shorten the reaction time and lower the cost by optimizing the formulation and reaction condition of SSZ-13, as well as introducing crystal seed or accelerant in SSZ-13.

1. Experiment

1.1 Equipments and reagents

(1) Equipments

100 mL self-made small reactor; oven; BD 90 XRD spectrometer from Peking University (CuK as diffraction source, 36 kV tube voltage, 16 mA tube current, 2θ range of 5~35°, step width = 0.02°, resolution < 60%, θ accuracy < 0.05°, 2θ accuracy < 0.01°); ST-3000P BET specific surface area meter from Beijing Rayleigh Analytical Instrument Co., Ltd. (high purity nitrogen as carrier gas and nitrogen as absorbent at the liquid nitrogen temperature); S-3500N SEM from Hitachi of Japan; ICP-AAS from PerkinElmer of US; BIO-RAD FT-IR spectrometer (resolution = 2 cm⁻¹, accumulation of 16 scans, solid sample: KBr = 1:160).

(2) Reagents

Silica sol: industrial first-grade, from Tianjin Jingling Electronic Material Technology Co., Ltd.; aluminum sulphate: analytically pure, from Tianjin Kermel Chemical Reagent Co., Ltd.; sodium hydroxide: analytically pure, from Tianjin Kermel Chemical Reagent Co., Ltd.; N, N, N-trimethyl-l-adamant ammonium hydroxide: from Johnson Matthey National Sales Office.

1.2 Preparation of SSZ-13 molecular sieve

SSZ-13 molecular sieve is prepared by the traditional hydrothermal method with silica sol, aluminium sulphate, sodium hydroxide and deionized water as raw material, and N, N, N-trimethyl-l-adamant ammonium hydroxide as a template. Mix SiO₂, A1₂O₃, Na₂O, R₂O and H₂O uniformly in the ratio of 40:1:16:5:900, age the mixture at room temperature for 0.5 h, then pour the mixture into a PTFE-lined high-pressure reactor, and crystallize at 155 for 2~5 days. SSZ-13 molecular sieve is then prepared by pouring the obtained crystal into beaker, heating it to 70~80 , drying the separated crystal at 120 after three cycles of ion exchange with a certain amount of ammonium chloride for 2 hours followed by vacuum filtration, and removing the template and water from the crystal by temperature-programmed calcinations.

2. Result and discussion

Figure 1 exhibits the standard XRD patterns of SSZ-13 molecular sieve reported by International Zeolite Association (IZA). Figure 2 exhibits the XRD spectra of SSZ-13 molecular sieve sample. Both figures exhibit the same features in peak position and peak shape. It indicates that the prepared crystal is a SSZ-13 molecular sieve without any mixed crystal.

2.1 Effects of the amount of sodium hydroxide on the preparation of SSZ-13 molecular sieve

Sodium hydroxide acts as a pH regulator in the preparation of SSZ-13 molecular sieve. The effects of alkalinity on the preparation of SSZ-13 molecular sieve are observed by altering the amount of sodium hydroxide. Figure 3 exhibits the XRD spectra of SSZ-13 molecular sieve prepared at different amount of sodium hydroxide (the ratio of n_{Na2O} to $n_{Al_2O_3}$ is 4, 8, 12, 16 and 20 respectively). From figure 3, we can see that the crystallinity increases with the rise of the alkalinity at the beginning, and reaches the maximum when the ratio of n_{Na2O} to $n_{Al_2O_3}$ is 16, however decreases rapidly when the alkalinity continues to increase, and forms a compact amorphous structure when the ratio of n_{Na2O} to $n_{Al_2O_3}$ is 20. Generally, the increase of alkalinity can promote the reaction, improve the solubility of silicon and aluminum, and change the polymerization state and distribution of raw materials in synthetic system, as well as accelerate the crystallizing speed, in turn shorten the induction period and nucleation period of crystallization. However, overhigh alkalinity leads to the overhigh solubility of silicon and aluminum, and the decline of crystallinity and specific surface area, in turn the formation of a compact amorphous structure. Therefore, either overhigh or overlow alkalinity has an adverse effect on the formation of crystal. In other words, SSZ-13 molecular sieve of high crystallinity can be obtained only in the proper alkalinity range.

2.2 Effects of the amount of water on the preparation of SSZ-13 molecular sieve

Water acts as a reaction medium and regulates the concentration of raw materials in the preparation of SSZ-13 molecular sieve. The effects of water on the preparation of SSZ-13 molecular sieve are observed by altering the amount of water. Figure 4 exhibits the XRD spectra of SSZ-13 molecular sieve prepared at different amount of water (the ratio of $n_{H_{2O}}$ to $n_{Al_{2O_3}}$ is 700, 900, 1100, 1350 and 1500 respectively). From figure 4, we can see that the crystallinity increases with the rise of the amount of water at the beginning, reaches the maximum when the ratio of $n_{H_{2O}}$ to $n_{Al_{2O_3}}$ is 900, and changes little until the ratio of $n_{H_{2O}}$ to $n_{Al_{2O_3}}$ is 1100, however decreases when the amount of water continues to increase. It is because the amount of water is associated with the concentrations of raw materials; in turn has an effect on the polymerization state and distribution of raw materials in synthetic system. In addition, the amount of water directly affects the change in alkalinity, in turn affects the preparation of SSZ-13 molecular sieve. Therefore, properly lowering the amount of water can increase the crystallinity of SSZ-13.

2.3 Effects of crystallization period on the preparation of SSZ-13 molecular sieve

Crystallization period has a great effect on the crystallinity of SSZ-13. The effects of crystallization period on the preparation of SSZ-13 molecular sieve are observed by altering the reaction time. Figure 5 exhibits the XRD spectra of SSZ-13 molecular sieve prepared within different periods of crystallization (from 1 day to 5 days). From figure 5, we can see that the crystallinity increases with the reaction going on at the beginning, and reaches the maximum on the 3rd day, then levels off and even decreases a little. It is because a too short period of crystallization leads to the formation of amorphous structure or mischcrystal, whereas a too long period of crystallization changes the originally formed pure crystal into other crystal. Therefore, either too long or too short period of crystallization has an adverse effect on the crystallinity of SSZ-13. Generally, without addition of any crystal seed or accelerant, the best crystallization period of SSZ-13 is 3 days.

2.4 Effects of accelerant on the preparation of SSZ-13 molecular sieve

The effects of accelerant on the preparation of SSZ-13 molecular sieve are observed by introducing a certain amount of accelerant into the reaction system. Figure 6 exhibits the XRD spectra of accelerant-contained SSZ-13 prepared within different periods of crystallization (from 1 day to 4 days). By comparing figure 6 with figure 5, we can see that the accelerant-contained SSZ-13 reveals an increase in crystallinity. It is probably because the accelerant speeds up the formation of silicon-oxygen tetrahedron oligomer and aluminum-oxygen tetrahedron oligomer, in turn accelerates the nucleation and growth of crystal (Kumar R *et al*, 1998, p. 23-31; Kumar R *et al*, 1996, p. 298-300). As a result, it rapidly forms the desired crystal on the 2^{nd} day.

2.5 Characterization of SSZ-13 molecular sieve

Figure 7 exhibits a SEM image of SSZ-13 molecular sieve sample. We can see a highly overlapped and irregular crystalline structure of SSZ-13 from it.

Figure 8 reveals the FT-IR spectra of SSZ-13 molecular sieve sample, which exhibits a T—O bending vibration band of silicon-oxygen tetrahedron or aluminum-oxygen tetrahedron at 530 cm⁻¹, a vibration band of double six-membered ring at 640 cm⁻¹, a symmetric vibration band of Al—O at 730 cm⁻¹, a very strong asymmetric stretching vibration band of O—Si—O or O—Al—O around 1000~1300 cm⁻¹, a N—H bending vibration band of ammonium ion at 1700 cm⁻¹, and a wide and strong band attributed to N—H stretching vibration of ammonium ion at 3400 cm⁻¹ which indicates a very strong acidity of SSZ-13 molecular sieve.

3. Conclusion

We have inclusively investigated the preparation conditions and influencing factors of SSZ-13 to achieve the best formulation: $SiO_2 /A1_2O_3=40$, $Na_2O /A1_2O_3=12\sim16$, $R_2O/A1_2O_3=5$, $H_2O/A1_2O_3=900\sim1100$. The SSZ-13 molecular sieve is then prepared by crystallizing the above mixture at 155 for either 3 days without addition of crystal seed and accelerant or 2 days in the presence of crystal seed and accelerant. This study not only shortens the crystallization period and lowers the preparation cost, but also increases the specific surface area and improves the catalysis property of the crystal. It indicates that the method studied here is valuable for broader applications and feasible for industrialization.

We have prepared SSZ-13 molecular sieve by the traditional hydrothermal method. There are many different options for raw materials in this case. For examples, you can select a silicon-contained compound from silica sol, silica gel, tetraethyl orthosilicate and etc., an aluminium-contained compound from aluminium oxide, pseudo-boehmite, aluminium hydroxide, aluminium sulphate and etc., and a template from N, N, N-trimethyl-l-adamant ammonium hydroxide, benzyl trimethyl ammonium hydroxide (Stephen J M *et al*, 2008, US 2008/0159950) and their mixture.

In addition, there are many other methods for preparing SSZ-13 molecular sieve (Stacey I Zones, 1985, US 4544538). For examples, it can be prepared with the porous matrix materials and mixed dot matrix materials such as the binary compounds including silica gel, aluminium oxide, titanium dioxide, magnesium oxide, Si-Al, Si-Mg, Si-Zr, Si-Th, Si-Be, Si-Ti and Ti-Zr, and the ternary compounds including Si-Al-Th, Si-Al-Zr, Si-Al-Mg and Si-Mg-Zr. In addition, it also can be prepared from other zeolites such as artificial and natural faujasite (Zones S I, 1991, p. 3709-3716), erionite, mordenite, pure artificial zeolites (for preparing ZSM molecular sieve, for example) and etc.

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Figure 1. Standard XRD pattern of SSZ-13 molecular sieve



Figure 2. XRD spectra of SSZ-13 molecular sieve sample



 $\label{eq:stars} The ratio of n_{Na2O} to n_{Al_{2O3}}: (1) 4; (2)8; (3)12; (4)16; (5)20 \\ Figure 3. XRD spectra of SSZ-13 molecular sieve prepared at different amount of sodium hydroxide \\$



The ratio of $n_{H_{2O}}$ to $n_{Al_{2O_3}}$: (1) 700; (2) 900; (3) 1100; (4) 1350; (5) 1500 Figure 4. XRD spectra of SSZ-13 molecular sieve prepared at different amount of water



Crystallization period: (1) 1 day; (2) 2 days; (3) 3 days; (4) four days; (5) five days Figure 5. XRD spectra of SSZ-13 molecular sieve prepared within different crystallization period



Crystallization period: (1) 1 day; (2) 2 days; (3) 3 days; (4) four days Figure 6. XRD spectra of accelerant-contained SSZ-13 prepared within different crystallization period



Figure 7. SEM image of SSZ-13 molecular sieve sample



Figure 8. FT-IR spectra of SSZ-13 molecular sieve sample