Hydrothermal Stability of Molecular Sieves SBA-15 Research

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ABSTRACT

Hydrothermal Stability of Molecular Sieves SBA-15 was studied. It was characterized by N\textsubscript{2} adsorption, X-ray diffraction and FT-IR analysis. The results indicated that water, heat and alkaline environments are acidic center caused some of the molecular sieve SBA-15, the influence of the structure of the SBA-15 mesoporous molecular sieves have some damage, led to the decrease of the pore diameter, specific surface area. This is because the thermal stability of mesoporous molecular sieve is closely related to the silicon hydroxyl condensation. Due to the contraction of silicon hydroxyl, generated the Si-O-Si unit structure, causes the d100. Moderate Si-OH condensation can increase the stability of mesoporous structure, and excessive Si-fuelled by condensation of Ozzie and Harriet channel by Si-O keys tensile force, spacing gradually reduced resulting in progressive collapse of mesoporous structure.

INTRODUCTION

Mesoporous molecular sieves with the rule of channel structure, high specific surface area, pore wall thickness, aperture, and the advantages of adjustable aperture makes uniform during the process, selective adsorption, chemical catalysis, biological function materials have a potential application value[1]. Using the SBA-15 channel limit action preparation of nanometer catalyst materials, introduces the performance of different atoms or molecules of pure silicon SBA-15 mesoporous molecular sieve, acidic and redox active center. With literature reports, the metal ion Al, Ti, Zr, etc.[2,3,4] is introduced into the

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SBA-15 skeleton and the pore, increase the SBA-15 mesoporous molecular sieve catalytic activity.

Stucky et al.[5] use after amination of different aperture of SBA-15 molecular sieve and MCF, and ionic strength of solution by controlling the implementation of different sizes of the separation of proteins. Zhao et al., using C18 modified molecular sieve SBA-15 as chromatographic column material, this material can be of different sizes of chromatographic separation of biomolecules. In addition, the SBA-15 mesoporous molecular sieve by measuring current and voltage, the formation of different biosensors, at the same time, in drug embedding and controlled release, biological chip[6] also has potential application value.

This paper studied the SBA-15 water heat resistance, tolerance under different pH conditions, etc., and carries on the metal oxide modified or modification.

**EXPERIMENTAL**

**SBA-15 Molecular Sieves preparation**

Hydrothermal synthesis method was used to tetraethyl silicate as silicon source, three block P123 as surfactant. In 40°C under the condition of constant temperature, the 6.0 g surfactant P123 and 150 ml deionized water to 250ml round bottom flask, magnetic stir until completely dissolved, add 90ml 4 mol/L HCl solution, in 40°C under the condition of constant temperature continue to stir, to mix solution, add 15ml are four ethyl silicate vinegar, continue to constant stirring for 24 h. And then transfer the mixture to Tenon tetrafluoroethylene for lining inside the autoclave, the crystallized under the condition of 100°C for 24 h, filtering hectares to supernatant fluid, with deionized water washing to neutral products, drying under 100°C for 24 h, after drying the product to the rate of 5°C /min from room temperature up to 550°C roasting 6h, namely getting white powdered SBA-15 mesoporous molecular sieve. Ni/SBA-15 catalyst used for volume impregnation method. According to SBA-15 impregnated by certain proportion to match good nickel nitrate in the solution.

**Catalyst Characterizations**

XRD patterns were recorded on a Rigaku D/max2250 powder X-ray diffraction with monochromated Cu-Kα (40kV/100mA) radiation. 2θ angles ranged from 10 to 80 with a speed of 8°/min. FT-IR spectra were recorded using a TENSOR27 spectrometer. The range in wave number was 400-4000cm⁻¹. The amount of carbon deposited on the catalysts was determined on a PerkinElmer TG/DTA instrument under air atmosphere.
RESULTS AND DISCUSSIONS

SBA-15 Molecular Sieve of Water Thermal Stability Test

SBA-15 molecular sieve by boiling water after 5d XRD spectrum is shown in figure 1. From XRD graph we can see that after 100°C boiling water treatment 5d, although its (100) crystal plane diffraction peak is visible, but the (110) and (200) crystal plane diffraction peak almost entirely disappeared. SBA-15 molecular sieve (100), (110) and (200) crystal plane diffraction peak with the increase of the water processing time and high Angle displacement, suggesting that boiling water processing SBA-15 will cause the contraction of hole wall.

SBA-15 5 d and 10 d water heat after infrared spectrum is shown in figure 2. By boiling water after 10 d, the skeleton near the 465 cm\(^{-1}\) Si-O-Si keys of bending vibration absorption peak, near 801 cm\(^{-1}\) Si-O tetrahedron of symmetric stretching vibration peak, near Si-O-Si1098 cm\(^{-1}\) tetrahedral anti symmetric telescopic characteristic peaks are still clear, but relatively pure SBA-15, the absorption strength are decreased significantly. And treatment after 10 d absorption intensity than the absorption intensity of weaker after 5 d. This suggests that the pure molecular sieve SBA-15 through 100°C water treatment 5 d and 10 d, while also keep a certain amount of structure, but the skeleton has collapsed, and with the increase of boiling time, the worse the collapse of the skeleton. And after the boil 10 d, its two-dimensional six-party structure considering the basic loss.

Figure 1. Low angle XRD patterns of Pure SBA-15 and SBA-15 with boiling water for different time.
(a) Pure SBA-15 (b) SBA-15 with boiling water for 5 days
(c) SBA-15 with boiling water for 10 days.
SBA-15 Molecular Sieve Stability in Acid and Alkali Environment

SBA-15 holes in the molecular sieve in the pH=10, 11, 12 basic NaOH solution boil after 48 hours the XRD spectrum, is shown in figure 3.

SBA-15 molecular sieve in the pH=10, 11, 12 alkaline boiling in NaOH solution after 48 hours the XRD spectrum. From figure 3, you can see that when SBA-15 in the alkali solution pH=12 treatment after 48 hours, the XRD spectrum (100), (110) and (200) crystal plane diffraction peak has basically does not exist. The processing in the alkali solution pH=12 after 48 hours, the two-dimensional six-party structure considering the basic loss. In the pH=10, pH=11 and under the condition of the (100) crystal plane diffraction peak is still there,
but the diffraction intensity decreased obviously, and the (110), (200) crystal plane diffraction almost entirely disappeared. In addition, the pH=11 diffraction intensity than the pH=10 diffraction intensity is much lower.

We are under the condition of fixed other conditions unchanged, SBA-15 mesoporous molecular sieves were studied in the pH=8,9, 10, 11, 12 alkaline boiling in NaOH solution after 48 hours, is shown in figure 4. In infrared image, with the increase of solution pH, the characteristic absorption peak, in turn, reduced, thus we can also get the same conclusion. Suggesting that treated by alkali solution SBA-15 mesoporous molecular sieves in our test conditions can still maintain the six-party channel structure, have a certain ability to resist the alkaline solution, but the SBA-15 molecular sieves are still sensitive to alkali solution, and the higher the pH, the greater the influence, under the condition of our test, pH greater than 10 above, almost can't keep its six-party channel structure. Small Angle XRD spectrum diagram, with the increase of pH, all infrared characteristic absorption peak of SBA-15, in turn, reduced, and the pH=12, 452cm⁻¹ near the skeleton of Si-O-Si key bending vibration absorption peak and near 1090cm⁻¹Si-O-Si tetrahedron anti symmetric telescopic characteristic peak basic disappear, pH=12 alkali solution. After 48 hours, the basic skeleton to collapse.

CONCLUSION

By hot water, alkaline solution after solution treatment of SBA-15 molecular sieve pore diameter smaller, XRD figure 27 width increases, the intensity is reduced, infrared absorption peak still exist, but the characteristic absorption peak intensity decreased significantly. Its structure with some damage, leads to a decrease in pore size and lower than that of the surface. Suggesting that SBA-15
molecular sieve in aqueous solution has a certain resistance to water thermal stability, but the structure will vary with the passage of time slowly collapse. In alkaline solution, the skeleton of the silicon atom has the tendency of dissolution, caused the decrease of the hole wall and the collapse of the partial skeleton, and the higher the alkaline solution pH, the impact become more serious.

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