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Article

Incorporation of Al^{3+} ions to promote the stabilization effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment on the hydrothermal stability of mesoporous SBA-15 zeolite

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ABSTRACT

This work demonstrates an improved $(\text{NH}_4)_2\text{SiF}_6$ treatment to enhance the hydrothermal stability of mesoporous SBA-15 zeolite. In this treatment, Al^{3+} ions are incorporated into SBA-15 zeolite first, then it is treated with 5% $(\text{NH}_4)_2\text{SiF}_6$ solution according to 1% SiO_2 of SBA-15 and finally washed with HCl (2 mol/L) to remove the pre-incorporated Al^{3+} ions. The obtained SBA-15 exhibits higher hydrothermal stability than that without pre-incorporated Al^{3+} . Compared with the latter, the sample maintains a better ordered mesostructure and a larger surface area ($271 \text{ m}^2/\text{g}$) after hydrothermal treatment at 800°C for 12 h in 100% steam. The results show that incorporating Al^{3+} ions into SBA-15 zeolite before $(\text{NH}_4)_2\text{SiF}_6$ treatment obviously promotes the stabilization effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment. The mechanism suggests that the incorporated Al^{3+} ions can effectively capture F^- ions that have been released from $(\text{NH}_4)_2\text{SiF}_6$, and thus reduce their etching into the SBA-15 zeolite framework. This ensures that the positive factors of $(\text{NH}_4)_2\text{SiF}_6$ treatment, such as silicon insertion and surface hydrophobization by F^- ions, play effective roles in the improvement of the hydrothermal stability of SBA-15 zeolite. This promoting effect of the Al^{3+} ions is closely related to the method that is used to introduce the Al^{3+} and the SBA-15 zeolite processing temperature.

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1. Introduction

Mesoporous SBA-15 zeolite has attracted much attention owing to its interesting mesostructure and wide application as a catalyst and support [1–6]. However, many catalytic reactions, such as oxidation, hydrogenation, dehydration, hydration and F-T synthesis reactions, are often carried out in the presence of H_2O or even in aqueous solution. Moreover, cracking catalysts are usually regenerated in steam at high temperature. Therefore, high hydrothermal stability is one of the most important features required of catalysts and supports [7–9]. Un-

fortunately, mesoporous silica has a poor hydrothermal stability. When heated in aqueous conditions or steam for long time, the material suffers from the collapse of its ordered mesostructure and a corresponding loss of surface area. Therefore, much research work has focused on improving the hydrothermal stability of mesoporous silica by various approaches, such as thickening of walls by adding inorganic salts or using some unusual surfactants [10,11], removing surface Si-OH groups by silylation [12–14] and F^- ions [15–17] to form a hydrophobic surface, crystallization at high temperature ($150\text{--}220^\circ\text{C}$) using thermally stable fluorine-containing sur-

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factants as templates [18], adjusting the solution pH = 1–3 to avoid the decomposition of the P123 copolymer [19], or employing carbon-propping and high temperature treatment at 800 °C [20] to enhance the silica condensation of the walls [18–26]. All of these methods have been successful in improving the hydrothermal stability of mesoporous SBA-15 zeolite, but some of them are difficult in operation and controlling conditions, and some are time and energy consuming, costly or environmentally unfriendly.

We previously reported a simple and low-energy consumption approach to improve the hydrothermal stability of SBA-15 zeolite via post-treatment with $(\text{NH}_4)_2\text{SiF}_6$ [7]. The modified SBA-15 zeolite exhibited good stability. Even after treatment at 800 °C for 12 h in 100% steam, its ordered mesostructure was still well maintained and had a high surface area of 213 m²/g. However, we also found that some F[−] ions released from $(\text{NH}_4)_2\text{SiF}_6$ can etch the framework of SBA-15 zeolite to form new Q₃ surface defects, as well as replace surface Si–OH groups to form a hydrophobic surface. Thus, the stabilization effect of the $(\text{NH}_4)_2\text{SiF}_6$ treatment on the hydrothermal stability of SBA-15 zeolite, the efficacy of which depends on the combined effect of both positive factors of silicon insertion and the surface hydrophobization by F[−] ions and the negative factor of F[−] ion etching, is weakened. Therefore, it is important to reduce the etching of F[−] ions for enhancing the stabilization effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment.

As known, the bond energy of Al–F is 665 kJ/mol, which is larger than that of Si–F (582 kJ/mol) and Al–O (585 kJ/mol); and the bond length of Al–F is 1.63×10^{-10} m, which is shorter than that of Si–F (1.71×10^{-10} m) and Al–O (1.75×10^{-10} m). This suggests that Al–F bonds have superior stability to those of Si–F and Al–O bonds. In other words, Al³⁺ ions have a stronger binding ability with F[−] ions than Si⁴⁺ ions do. Therefore, it is possible that using Al³⁺ ions to capture F[−] ions will reduce the amount of etching by F[−] ions and promote the stabilization effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment on the hydrothermal stability of SBA-15 zeolite.

In this research, we demonstrate an improved $(\text{NH}_4)_2\text{SiF}_6$ treatment to enhance the hydrothermal stability of mesoporous SBA-15 zeolite by incorporating Al³⁺ ions into the SBA-15 before the $(\text{NH}_4)_2\text{SiF}_6$ treatment, then washing the sample with HCl (2 mol/L) to remove the Al³⁺ ions. The obtained SBA-15 zeolite displayed higher hydrothermal stability than that without incorporated Al³⁺, evaluated using hydrothermal treatment at 800 °C for 12 h in 100% steam. The promotion mechanism of Al³⁺ ions, as well as the influence of the method of Al³⁺ introduction, is also discussed according to X-ray diffraction (XRD), N₂ adsorption, ²⁹Si and ²⁷Al NMR, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) characterizations.

2. Experimental

2.1. Chemicals

Triblock copolymer EO₂₀PO₇₀EO₂₀ (P123, Aldrich, Milwaukee, WI, USA, M_r = 5800), aluminum isopropoxide (Lingfeng

Chemical Corp., Shanghai, China, analytical grade), tetraethyl orthosilicate (TEOS, Aldrich, analytical grade, 98%), ammonium fluorosilicate (NH_4SiF_6), ammonium acetate (NH_4Ac), and hydrochloric acid (Shanghai Chemical Corp., Shanghai, China, analytical grade) were used as received without any further purification.

2.2. Sample synthesis

SBA-15 and AlSBA-15 zeolites were synthesized according to Refs. [27] and [28], respectively. S15-*x*%SiF and AlS15-*x*%SiF samples were prepared according to Ref. [7]. In a typical procedure, 3 g of calcined SBA-15 or AlSBA-15 were dispersed in 90 mL of NH_4Ac solution (0.3 mol/L). The defined amount of $(\text{NH}_4)_2\text{SiF}_6$ solution (5%) was then dropped into the mixture under vigorous stirring at 60 °C. After 1 h, the solution was filtrated, and the solid was washed twice and dried at 120 °C for 4 h. In the sample names, “*x*” denotes the SiO₂ ratio of $(\text{NH}_4)_2\text{SiF}_6$ to SBA-15 or AlSBA-15.

S15-(1%SiF+1%Al) was prepared in the same manner as S15-*x*%SiF, except 1% of AlCl₃ (mole ratio of Al to SiO₂ in the SBA-15) was dissolved in 90 mL NH_4Ac (0.3 mol/L) before the defined amount of $(\text{NH}_4)_2\text{SiF}_6$ solution was added.

S15-1%SiF/1%Al was prepared from S15-1%SiF with the impregnation of 1% AlCl₃ (pH = 2.0 solution). It was dried at 120 °C for 4 h before use.

AlS15-1%SiF-DAl was prepared by washing 1 g of AlS15-1%SiF twice in 10 mL of HCl (2 mol/L) solution under stirring at 80 °C for 2 h, after which the sample was washed to pH = 7 and dried at 120 °C for 4 h.

2.3. Evaluation of hydrothermal stability

All samples were treated hydrothermally in a tube furnace at 800 °C for 12 h under a gas flow (1000 mL/min) of 100% steam.

2.4. Characterization

XRD patterns were recorded on a Bruker D8 X-ray diffractometer (Germany) with Ni-filtered Cu K_α radiation (40 kV, 40 mA). N₂ adsorption-desorption isotherms were measured at −196 °C with a Micromeritics Tristar 3000 analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of the samples using adsorption data in a relative pressure range from 0.05 to 0.2. Pore size distributions (PSDs) were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume V_t was estimated from the amount adsorbed at a relative pressure p/p_0 of 0.995. The microporous volume V_{micro} was analyzed with $V-t$ plots. TEM and SEM images were obtained using a JEOL 2011 microscope operated at 200 kV and a Philip XL30 instrument, respectively. ²⁷Al and ²⁹Si NMR spectra were measured on a Bruker AVANCE 400MHz spectrometer. ²⁹Si NMR was performed at a frequency of 59.621 MHz, a recycling delay of 600 s, a radiation frequency intensity of 62.5 kHz, and with a Q₈M₈ reference sample ($((\text{CH}_3)_3\text{SiO})_8\text{Si}_8\text{O}_{12}$).

3. Results and discussion

3.1. Influence of incorporated Al^{3+} on the stabilization effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment

The XRD patterns (Fig. 1(a)) of SBA-15, S15-1%SiF, and AIS15-1%SiF-DAL display three well-resolved diffraction peaks at $2\theta = 0.9^\circ$ and 1.5° – 2.0° , corresponding to the (100), (110), and (200) reflections of the 2D hexagonal mesostructure of SiO_2 . All of the samples exhibited typical type IV isotherms comprising a H_1 -type hysteresis loop (Fig. 2(a)) and had a fibrous morphology with well-ordered hexagonal mesostructure (Fig. 3). These results suggest that the $(\text{NH}_4)_2\text{SiF}_6$ treatment, the incorporation of Al^{3+} ions and the subsequent dealumination by washing with HCl solution did not destroy the ordered mesostructure. However, Table 1 shows that the surface areas of S15-1%SiF and AIS15-1%SiF-DAL decreased to 490 and 497 m^2/g from 878 m^2/g of the SBA-15 zeolite, respectively; their pore volumes dropped to 0.81 and 0.72 cm^3/g from 1.3 cm^3/g , respectively; and their pore diameters were reduced to 6.9 and 5.9 nm from 7.1 nm, respectively. As shown in the XRD patterns, the (100) diffraction peak of the three samples had the same 2θ ($= 0.9^\circ$), suggesting that they had the same unit cell

parameters, so the decrease in pore diameter implies that the mesoporous walls of S15-1%SiF and AIS15-1%SiF-DAL had thickened. As suggested by our previous work [7], during $(\text{NH}_4)_2\text{SiF}_6$ treatment, Si atoms can insert into the framework of SBA-15 zeolite to repair surface defects, resulting in the closure of most of the micropores, and SiO_2 can deposit on the walls and block mesopores and micropores. These processes may have caused the surface area, pore volume and diameter of S15-1%SiF and AIS15-1%SiF-DAL to decrease drastically from those of SBA-15.

After SBA-15 zeolite was treated hydrothermally at 800 $^\circ\text{C}$ for 12 h in 100% steam, its characteristic diffraction peaks at $2\theta = 0.9^\circ$ and 1.5° – 2.0° (Fig. 1(b-1)) and typical H_1 -type hysteresis loop (Fig. 2(b-1)) disappeared completely. Its fibrous morphology collapsed, and no ordered mesopores were observed in SEM and TEM images (Fig. 3), while its surface area was reduced to 71 m^2/g . These results suggest that the ordered mesostructure of the hydrothermally treated SBA-15 zeolite had been destroyed. However, the S15-1%SiF sample subjected to the same hydrothermal treatment still exhibited a (100) reflection diffraction peak at $2\theta = 0.9^\circ$ and a distorted H_1 -type hysteresis loop (Fig. 2(b-2)). Some ordered mesostructuring and a loose fibrous morphology were also observed in SEM and

Fig. 1. XRD patterns of SBA-15 (1), S15-1%SiF (2), AIS15-1%SiF-DAL (3), AIS15-1%SiF (4), and AISBA-15 (5) samples before (a) and after (b) hydrothermal treatment at 800 $^\circ\text{C}$ for 12 h in 100% steam.

Fig. 2. N_2 adsorption isotherms of SBA-15 (1), S15-1%SiF (2), AIS15-1%SiF-DAL (3), AIS15-1%SiF (4), and AISBA-15 (5) samples before (a) and after (b) hydrothermal treatment at 800 $^\circ\text{C}$ for 12 h in 100% steam.

Fig. 3. SEM (left) and TEM (right) images of SBA-15 (A), S15-1%SiF (B), AIS15-1%SiF-DAl (C), AIS15-1%SiF (D), and AISBA-15 (E) samples before (a) and after (b) hydrothermal treatment at 800 °C for 12 h in 100% steam.

TEM images. The sample retained a high surface area of 224 m²/g. These results indicate that S15-1%SiF had a higher hydrothermal stability than SBA-15, which is in good agreement with our previous work [7].

Notably, the AIS15-1%SiF-DAl sample treated hydrothermally at 800 °C for 12 h in 100% steam had some significant differences to the S15-1%SiF sample: (1) the (100) reflection peak at $2\theta = 0.9^\circ$ had higher intensity, while the diffraction peaks of the (110) and (200) reflections at $2\theta = 1.5^\circ$ – 2.0° were less distinct; (2) its H₁-type hysteresis loop was less distorted; (3) the fibrous morphology and ordered mesostructure were better maintained; (4) a higher surface area of 271 m²/g and bigger pore volume of 0.53 m³/g were maintained. All of these results indicate that AIS15-1%SiF-DAl has a higher hydrothermal stability than S15-1%SiF.

To prevent framework Al from affecting the hydrothermal stability of the SBA-15, the incorporated Al³⁺ ions in the AIS15-1%SiF-DAl sample were removed by washing with HCl solution after the (NH₄)₂SiF₆ treatment. As shown in Table 1, the Si/Al ratio of the AIS15-1%SiF-DAl sample was 380, which is close to that of SBA-15 (Si/Al = 487). Comparing this with the Si/Al ratio (Si/Al = 78) of the AIS15-1%SiF sample before dealumination by HCl, it is calculated that about 80% of the

incorporated Al³⁺ ions were removed by the acid wash process. Although about 20% of the framework Al still existed in this sample, we believe that these Al atoms had little contribution to the hydrothermal stability, because AISBA-15, which had more framework Al (Si/Al = 69) than AIS15-1%SiF-DAl, had a surface area of just 177 m²/g and a weak (100) diffraction peak after hydrothermal treatment. Thus, it showed worse hydrothermal stability than AIS15-1%SiF-DAl. Therefore, we propose that the high hydrothermal stability of AIS15-1%SiF-DAl is related to a synergistic effect of the incorporated Al³⁺ ions that promoted the stabilization effect of (NH₄)₂SiF₆ treatment.

This result poses the question of whether AIS15-1%SiF would have higher hydrothermal stability than AIS15-1%SiF-DAl if the incorporated Al³⁺ ions were not removed by washing with HCl solution. However, the sample treated hydrothermally at 800 °C for 12 h in 100% steam only retained a surface area of 78 m²/g, and no diffraction peaks or H₁-type hysteresis loops were observed in its XRD pattern and N₂ adsorption-desorption isotherm, respectively. These results suggest that the hydrothermal stability of this sample was not improved at all by the incorporation of framework Al and (NH₄)₂SiF₆ treatment. On the contrary, the stabilization effect of the (NH₄)₂SiF₆ treatment observed for the S15-1%SiF sample was shielded by the incorporated Al. Unusually, this indicates that the incorporated Al³⁺ ions and (NH₄)₂SiF₆ treatment have different synergy and influence the hydrothermal stability of SBA-15 zeolite differently. The mechanism will be discussed below.

3.2. Influence of the amount of (NH₄)₂SiF₆ in the presence of incorporated Al³⁺ ions

As shown in Fig. 4, the surface areas of the S15-x%SiF samples were first maintained at around 490 m²/g and then decreased with increasing amount of (NH₄)₂SiF₆ above 4%. The samples displayed a similar variation in surface area after hydrothermal treatment at 800 °C for 12 h in 100% steam. These results indicate that treatment with more (NH₄)₂SiF₆ cannot enhance its stabilization effect further, which is in good agreement with our previous work [7]. This is because more F[−] ions are produced when an excess of (NH₄)₂SiF₆ is used. These can aggravate the etching into the framework of SBA-15 zeolite and form a greater amount of new surface defects.

However, AIS15-x%SiF-DAl and S15-x%SiF exhibited different relationships between surface area and amount of (NH₄)₂SiF₆. Before they were treated hydrothermally at 800 °C for 12 h in 100% steam, all of the samples had surface areas of

Table 1
N₂ adsorption data of various SBA-15 samples modified by (NH₄)₂SiF₆ before and after hydrothermal treatment at 800 °C for 12 h in 100% steam.

Sample	Before hydrothermal treatment						After hydrothermal treatment					
	Si/Al	<i>A</i> _{BET} (m ² /g)	<i>A</i> _{micro} (m ² /g)	<i>V</i> _t (cm ³ /g)	<i>V</i> _{micro} (cm ³ /g)	<i>D</i> _{BH} (nm)	Si/Al	<i>A</i> _{BET} (m ² /g)	<i>A</i> _{micro} (m ² /g)	<i>V</i> _t (cm ³ /g)	<i>V</i> _{micro} (cm ³ /g)	<i>D</i> _{BH} (nm)
SBA-15	487	878	213	1.30	0.34	7.1	—	71	2	0.26	0.02	—
S15-1%SiF	—	490	30	0.81	0.19	6.9	—	224	35	0.45	0.09	5.6
AIS15-1%SiF-DAl	380	497	60	0.72	0.19	5.9	—	271	27	0.53	0.10	5.6
AIS15-1%SiF	78	494	47	0.77	0.19	6.1	—	78	0	0.18	0.03	—
S15-(1%SiF+1%Al)	351	745	82	1.14	0.28	7.0	—	62	3	0.22	0.02	—
S15-1%SiF/1%Al	—	—	—	—	—	—	—	125	17	0.35	0.05	—
AISBA-15	69	551	66	0.75	0.21	6.2	—	177	0	0.42	0.06	—

Fig. 4. BET surface area of S15-*x*%SiF (a) and AIS15-*x*%SiF-DAL (b) samples before (1) and after (2) hydrothermal treatment at 800 °C for 12 h in 100% steam as a function of (NH₄)₂SiF₆ content.

about 500 m²/g. The surface areas of the AIS15-*x*%SiF-DAL samples did not decrease as the amount of (NH₄)₂SiF₆ was increased, unlike the S15-*x*%SiF samples. The surface areas of the hydrothermally treated AIS15-*x*%SiF-DAL samples only decreased slightly with increasing amount of (NH₄)₂SiF₆ compared with those of the corresponding S15-*x*%SiF samples, and remained above 230 m²/g. This result suggests that SBA-15 zeolites containing Al³⁺ ions can withstand a wide range of conditions of (NH₄)₂SiF₆ treatment. This may be because the incorporated Al³⁺ ions can prevent the etching of the SBA-15 zeolite framework by F⁻ ions. When treating SBA-15 zeolites without incorporated Al³⁺ ions, we often need to carefully control conditions such as the temperature, (NH₄)₂SiF₆ concentration, and (NH₄)₂SiF₆ solution dropping speed, to retard or avoid F⁻ ion etching. Now, the (NH₄)₂SiF₆ treatment procedure can be simplified by first incorporating Al³⁺ ions into the SBA-15.

3.3. Influence of method of Al³⁺ introduction

The S15-(1%SiF+1%Al) sample exhibited a surface area of 745 m²/g and a pore volume of 1.14 cm³/g (Table 1), which were very close to those of SBA-15. After hydrothermal treatment at 800 °C for 12 h in 100% steam, the S15-(1%SiF+1%Al) sample retained a surface area of just 62 m²/g, which is lower than that of S15-1%SiF sample (224 m²/g) and close to that of SBA-15 zeolite subjected to the same hydrothermal treatment. Thus, S15-(1%SiF+1%Al) had worse hydrothermal stability than S15-1%SiF and a similar one to that of SBA-15 zeolite. For this sample, although Al³⁺ ion incorporation did not promote the (NH₄)₂SiF₆ treatment, (NH₄)₂SiF₆ treatment did not exhibit a stabilizing effect.

In fact, this sample contained almost no aluminum. As shown in Table 1, the Si/Al ratio of the S15-(1%SiF+1%Al) sample was 351, close to that of SBA-15 zeolite (Si/Al = 487). This indicates that the AlCl₃, which was dissolved in NH₄Ac solution, was not incorporated into SBA-15 effectively. Instead, the Al was washed from the sample completely during (NH₄)₂SiF₆ treatment, so no promotion by Al³⁺ ions occurred.

Fig. 5. Mechanism of stabilization by (NH₄)₂SiF₆ treatment on the hydrothermal stability of SBA-15 zeolite under the assistance of incorporated Al³⁺ ions.

(NH₄)₂SiF₆ treatment did not render a stabilizing effect in this sample because the method of introducing Al³⁺ ions has great influence on the synergy with (NH₄)₂SiF₆ treatment. Directly introducing Al³⁺ into the same solution as the (NH₄)₂SiF₆ treatment is detrimental to the stabilization effect of the (NH₄)₂SiF₆ treatment. The mechanism will be discussed below.

3.4. Mechanism of Al³⁺ ion influence

As known from the bond energy data, Al³⁺ has a stronger binding ability with F⁻ than Si⁴⁺. Therefore, when SBA-15 zeolite was first modified with Al³⁺ ions, then treated with (NH₄)₂SiF₆ solution, the incorporated Al³⁺ ions acted to “capture” F⁻ ions (Fig. 5 (b-2)) and reduced the F⁻ etching of the SBA-15 zeolite framework (Fig. 5(a-1)). The role of the Al³⁺ ions is further confirmed by the following two facts.

First, Table 1 shows that the Si/Al ratio of the AISBA-15 sample was 69. The characteristic peaks of tetrahedral framework Al and octahedral extra-framework Al appeared at $\delta = 53.3$ and 0 in the ²⁷Al NMR spectrum of this sample (Fig. 6(1)), respectively. After treatment with (NH₄)₂SiF₆ solution, the Si/Al ratio of the AIS15-1%SiF sample increased to 78. The characteristic peak of octahedral extra-framework Al at $\delta = 0$ disap-

Fig. 6. ²⁷Al NMR spectra of AISBA-15 (1), AIS15-1%SiF (2), AIS15-1%SiF-DAL (3), AIS15-1%SiF-600-2h (4), and AIS15-1%SiF-700-2h (5) samples.

peared (Fig. 6(2)), and the peak of tetrahedron framework Al decreased slightly. This result suggests that some incorporated Al^{3+} ions, especially the extra-framework Al, were removed during the $(\text{NH}_4)_2\text{SiF}_6$ treatment because of their reaction with F^- ions to form soluble $[\text{AlF}_6]^{3-}$ ions.

Second, the ^{29}Si NMR spectra (Fig. 7) show that the $Q_4/(Q_3+Q_2)$ ratio of SBA-15 zeolite was 0.21. After treated with $(\text{NH}_4)_2\text{SiF}_6$ solution, the S15-1%SiF sample exhibited a slightly high ratio of $Q_4/(Q_3+Q_2) = 0.26$. During $(\text{NH}_4)_2\text{SiF}_6$ treatment, Si atoms can insert into the framework of SBA-15 zeolite and repair its surface defects to form the Q_4 structure from the Q_3 and Q_2 structures. Meanwhile, F^- ions released from $(\text{NH}_4)_2\text{SiF}_6$ can etch the SBA-15 zeolite framework to form new Q_3 or Q_2 surface defects. The combination of these two competitive factors caused the amount of Q_4 structure ($\text{Si}(\text{OSi})_4$) to increase by about 23.8%. However, when the AISBA-15 sample was treated with $(\text{NH}_4)_2\text{SiF}_6$, the preincorporated Al^{3+} ions acted as a “trap” for F^- ions and reduced the F^- etching into the SBA-15 zeolite framework. Combined with a small amount of direct Si insertion which repaired surface defects, the $Q_4/(Q_2+Q_3)$ ratio of AIS15-1%SiF markedly increased from the 0.34 of AISBA-15 to 0.54.

In the case of the AIS15-1%SiF-DAL sample, most of its framework Al was removed by washing with HCl (2 mol/L) via a process of dealumination. Thus, Si–O–Al and Si–O–Al–O–Si bonds were broken to form new Si–OH and (Si–OH+HO–Si) defects. As a result, the $Q_4/(Q_2+Q_3)$ ratio of this sample decreased to 0.37. Even so, the amount of Q_4 structure ($\text{Si}(\text{OSi})_4$) in this sample was still about 76.2% higher than that of SBA-15 zeolite, which is also higher than that of the S15-1%SiF sample. Although about 20% of the Al^{3+} ions still remained in the framework of the sample, they at most contributed about 12% of the amount of Q_4 , calculated from both the Si/Al and $Q_4/(Q_3+Q_2)$ ratios of the AIS15-1%SiF-DAL and AISBA-15 samples. Even if this part of the contribution to Q_4 is deducted, the amount of Q_4 structure was still increased by as much as 64.2% by the $(\text{NH}_4)_2\text{SiF}_6$ treatment. Obviously, with the same $(\text{NH}_4)_2\text{SiF}_6$ treatment, AIS15-1%SiF-DAL had a greater increase in Q_4 structure than S15-1%SiF without incorporated Al. This

result indicates that the incorporated Al^{3+} ions did capture F^- ions and slow their etching of the framework of SBA-15, such that the ability of $(\text{NH}_4)_2\text{SiF}_6$ to repair the surface defects of the silica appeared to be enhanced.

For the S15-(1%SiF+1%Al) sample, Al^{3+} ions introduced directly into the NH_4Ac solution did not have any promotion effect on the $(\text{NH}_4)_2\text{SiF}_6$ treatment. The reason for this is also the strong ability of Al^{3+} ions to capture F^- ions. AlCl_3 dissolves well in NH_4Ac solution and can quickly react with the dropped $(\text{NH}_4)_2\text{SiF}_6$ to form $[\text{AlF}_6]^{3-}$ ions, causing the $(\text{NH}_4)_2\text{SiF}_6$ to quickly decompose. Once the $(\text{NH}_4)_2\text{SiF}_6$ decomposed, it no longer had the ability to repair the surface defects of the SBA-15 zeolite. Moreover, there were not enough F^- ions in solution to replace the surface Si–OH groups to form a hydrophobic surface because most of them had been captured to form the stable $[\text{AlF}_6]^{3-}$ ions. Indeed, the dropped $(\text{NH}_4)_2\text{SiF}_6$ did not react with the SBA-15, but with Al^{3+} ions in the solution, resulting in it appearing that the sample had not been treated with ammonium fluorosilicate at all. Therefore, the surface area, pore volume, and Si/Al ratio of the S15-(1%SiF+1%Al) sample, as well as its hydrothermal stability, were very close to those of the original SBA-15 zeolite.

In the cases of the AIS15-1%SiF and AIS15-1%SiF-DAL samples, Al^{3+} ions were incorporated into the SBA-15 zeolite before the $(\text{NH}_4)_2\text{SiF}_6$ treatment. Thus, they existed as framework Al or as amorphous Al_2O_3 in the channels. Because neither of these aluminum species were free, unlike AlCl_3 in the solution, they could not react quickly with the dropped $(\text{NH}_4)_2\text{SiF}_6$, but effectively captured nearby excess F^- ions which had not reacted with Si–OH groups (Fig. 5(b-2)). Thus, the etching of the SBA-15 zeolite framework by F^- ions was retarded effectively. According to the above analysis, both AIS15-1%SiF and AIS15-1%SiF-DAL should have higher hydrothermal stability than S15-1%SiF sample. However, the AIS15-1%SiF sample showed a worse stability when treated hydrothermally at 800 °C. We believe that this is associated with the thermal stability of framework Al.

The AIS15-1%SiF sample was calcined at 600 and 700 °C for 2 h. The resulting samples AIS15-1%SiF-600-2h and AIS15-1%SiF-700-2h exhibited the characteristic peak of octahedral extra-framework Al at $\delta = 0$ in Fig. 6(4) and (5), and the intensity of the peak increased with the calcination temperature. This suggests that some framework Al was removed at high temperature to form amorphous Al. The higher the temperature, the more obvious this trend was. When AIS15-1%SiF was hydrothermally treated at 800 °C, some framework Al was removed to form extra-framework Al. These species strongly interact with F^- ions and can break Si–F bonds on the sample surface to form Al and F compounds (Fig. 5(c-1)). As a result, the hydrophobic effect obtained from Si–F bonds was weakened significantly. Moreover, the compounds of Al and F may have decomposed again and released some HF that further etched the silica framework during the hydrothermal treatment. These two negative effects caused the AIS15-1%SiF sample to show poor hydrothermal stability at 800 °C.

To confirm this conclusion, S15-1%SiF/1%Al, which was prepared from S15-1%SiF by impregnation with 1% AlCl_3 , was

Fig. 7. ^{29}Si NMR spectra of SBA-15 (1), S15-1%SiF (2), AISBA-15 (3), AIS15-1%SiF (4), AIS15-1%SiF-DAL (5), AIS15-1%SiF-600-2h (6), and AIS15-1%SiF-700-2h (7) samples.

treated hydrothermally at 800 °C for 12 h in 100% steam. Table 1 shows that the sample retained a surface area of only 125 m²/g, lower than that of S15-1%SiF (224 m²/g). This result proves that the presence of extra-framework Al in the channels does weaken the hydrothermal stability of SBA-15 zeolite treated with (NH₄)₂SiF₆.

Interestingly, we found that when AlS15-1%SiF was treated hydrothermally at a low temperature of 190 °C for 5 d in a closed vessel, it retained the highest surface area (result not listed here) compared with those of the S15-1%SiF and AlS15-1%SiF-DAI samples. The hydrothermal stability had good correlation with the ratio $Q_4/(Q_3+Q_2)$. This is because the framework Al was stable at temperatures less than 550 °C, and could not be removed to react with the surface Si–F bonds at 190 °C. This suggests that we must pay attention to the temperature at which SBA-15 materials containing Al³⁺ ions are used. If they are required undergo high temperature processes above 550 °C, such samples must be dealuminated after they are treated with (NH₄)₂SiF₆.

AlSBA-15 materials only contain weak Lewis acid sites, and cannot completely replace USY zeolite as an acid catalyst. However, AlSBA-15 materials have some ability to crack large molecules, so it can be used as an acid catalyst with microporous zeolites. Thus, some advantages of AlSBA-15 sample become apparent, for example, precracking of heavy molecules to form slightly smaller molecules, enhancement of the diffusion of reactants to the surface of microporous zeolites, and providing free mesoporous channels for the cracking products to quickly escape from the surface of USY zeolite to prevent them from being excessively cracked. It has been reported [5] that a NiW supported catalyst prepared from core-shell USY zeolite and AlSBA-15 material showed higher conversion and better selectivity in the cracking of heavy petroleum feedstocks than commercial catalysts prepared from USY zeolite. The catalyst also displayed a high stability in a pilot scale hydrocrack-

ing test of Iran VGO-2 with 200 mL of catalyst. During 800 h running, the reaction temperature was increased by just 1 °C to keep the conversion of the >370 °C fraction of the feedstock at approximately 68.5%. Although the present modified SBA-15 zeolite may still have worse hydrothermal stability than microporous zeolites such as USY and ZSM-5, we think that the obtained improvement is very important to ensure the practical application of SBA-15 zeolite as a catalyst support for the hydrocracking of heavy oil.

4. Conclusions

Mesoporous SBA-15 zeolite containing preincorporated Al³⁺ ions exhibited higher hydrothermal stability after treatment with (NH₄)₂SiF₆ solution and washing with HCl solution to remove the incorporated Al³⁺ than SBA-15 without incorporated Al³⁺. The incorporated Al³⁺ ions reduce the etching of the silica framework of SBA-15 by F⁻ ions, and effectively promote the positive effect of (NH₄)₂SiF₆ treatment on the hydrothermal stability of the SBA-15. Moreover, the incorporation of Al³⁺ ions leads to the (NH₄)₂SiF₆ treatment becoming simpler and easier to control. Therefore, the present approach has potential application in laboratory and industry to prepare ordered mesoporous silicas with high hydrothermal stability.

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Graphical Abstract

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Incorporation of Al³⁺ ions to promote the stabilization effect of (NH₄)₂SiF₆ treatment on hydrothermal stability of mesoporous SBA-15 zeolite

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An improved (NH₄)₂SiF₆ treatment by pre-incorporating with Al³⁺, which can capture F⁻ and reduce its etching into SBA-15 framework, finally promote the stabilization effect of (NH₄)₂SiF₆ treatment on SBA-15 zeolite.

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Al³⁺离子介入提升(NH₄)₂SiF₆对SBA-15介孔材料的水热稳定化作用

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摘要: 提出了一种(NH₄)₂SiF₆处理提高SBA-15介孔材料水热稳定性的改良方法. 采用SBA-15介孔材料中预引入Al³⁺离子, 再进行1%SiO₂计量的(NH₄)₂SiF₆处理, 最后用强酸洗脱预引入的Al³⁺. 结果显示, 由此处理的SBA-15材料, 其水热稳定性明显优于相同条件下未预引入Al³⁺时(NH₄)₂SiF₆处理的样品. 两者在800 °C、100%水蒸气处理12 h后, 虽然均能很好保持其介观有序度、形貌及六方孔道结构, 但前者的比表面积可高达271 m²/g, 而后者仅为224 m²/g. 表明Al³⁺离子介入能大幅度提升(NH₄)₂SiF₆处理对SBA-15介孔材料的稳定化作用. 这主要得益于预引入的骨架Al³⁺在保障(NH₄)₂SiF₆处理修复SBA-15材料表面缺陷和进行表面疏水化、提升其水热稳定性的同时, 能减缓(NH₄)₂SiF₆释放的多余F⁻离子对SBA-15材料骨架的刻蚀破坏作用. Al³⁺离子介入的这种提升作用与其引入方式和SBA-15材料所经受的温度密切相关.

关键词: SBA-15沸石介孔材料; 水热稳定性; 氟硅酸铵; Al³⁺离子引入; 补硅

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