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Modification of nanocrystalline HZSM-5 zeolite with tetrapropylammonium hydroxide and its catalytic performance in methanol to gasoline reaction

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ABSTRACT

Nanocrystalline ZSM-5 zeolite was modified with tetrapropylammonium hydroxide (TPAOH) solution. The effect of the TPAOH treatment time on the catalytic performance of HZSM-5 was investigated in methanol to gasoline (MTG) reaction. The modified samples were characterized using X-ray diffraction, scanning electron microscopy, ²⁷Al and ²⁹Si magic-angle spinning nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, N₂ adsorption, and NH₃ temperature-programmed desorption. The HZSM-5 structure was basically unchanged after modification, but the relative crystallinity increased and the crystal morphology was more regular. The Brunauer-Emmett-Teller surface area, the micropore surface area, the surface Si/Al ratio, and the amount of strong acid sites increased; this might be caused by desilication and dealumination, and secondary crystallization of the zeolite during the treatment. The stability of the catalyst was significantly improved after modification, as reflected by the increased lifetime from 70 h to above 170 h in MTG reaction. The catalyst lifetime increased with increasing TPAOH treatment time. Hydrogen transfer reactions became faster and led to more isoparaffins and less olefins in the liquid products.

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1. Introduction

The methanol to gasoline (MTG) process [1–3] was first discovered and developed by researchers at Mobil in 1976, based on coal or natural gas as the raw material and conversion of synthesis gas to methanol. In the MTG process, crude methanol is transformed into high-octane and high-quality gasoline, which contains no sulfur, chlorine, or other impurities and has a good anti-knock performance. With the shortage of world oil resources and the overproduction of domestic methanol,

methanol is becoming a new source of fossil-fuel raw materials.

ZSM-5 zeolite is usually used as the catalyst in the MTG process. The ZSM-5 zeolite framework contains two interconnected pore systems, i.e., straight channels (0.51 nm × 0.55 nm) and zigzag channels (0.53 nm × 0.56 nm), creating a three-dimensional network. The presence of micropores gives rise to the use of zeolites as shape-selective catalysts. In ZSM-5, diffusion of molecules that have a greater critical size than that of durene is difficult, leading to high selectivity in MTG. However, the stability of the parent HZSM-5 is not satisfactory be-

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cause of easy coke deposition on the strong acid sites on the surface [4]. It is therefore important to improve the catalyst stability.

Alkaline modification, i.e., desilication by treatment in an alkaline medium, is a very suitable and reproducible method for obtaining mesoporous ZSM-5 zeolites with improved diffusivity and catalytic cracking ability, and has attracted growing interest in zeolite applications in recent years. Currently, an inorganic NaOH solution is generally used as the alkaline medium. Bjørgen et al. [5] reported a significant improvement in the catalyst lifetime and a strongly enhanced selectivity towards the desired gasoline fraction, i.e., more aromatic and paraffinic compounds in the products, for HZSM-5 samples treated with NaOH solution. The results were rationalized by the development of acidity, improved crystallinity, and mesopore formation. Ogura et al. [6] and Suzuki et al. [7] found changes in the adsorption curves and pore size distributions for MFI zeolites modified with NaOH solution, leading to increased catalytic activity. Groen et al. [8,9] reported the formation of accessible intracrystalline mesopores in HZSM-5 as a result of selective removal of framework silicon by controlled desilication with NaOH. Ni et al. [10] prepared a hierarchical mesoporous Zn/ZSM-5 zeolite catalyst by NaOH treatment and Zn impregnation, giving significant improvements in the catalyst lifetime and liquid hydrocarbon yield in the MTG reaction. Xiao et al. [11] studied NaOH-treated mordenite containing a template and obtained increased isobutene conversion for ethyl *tert*-butyl ether synthesis. At present, organic alkaline treatment is usually used for TS-1. Compared with inorganic alkaline treatments, organic alkaline treatments give more moderate modifications and are more easily controlled. Mao et al. [12] found that the structure of TS-1 was basically unchanged after modification with tetrapropylammonium hydroxide (TPAOH) solution, but internal corrosion occurred. The modified sample showed a significant improvement in catalytic performance in the hydroxylation of phenol and ammoxidation of methyl ethyl ketone. Xia [13] studied TPAOH-treated TS-1 and observed an improved performance in the ammoxidation of methyl ethyl ketone. To date, few organic alkaline modifications of ZSM-5 zeolites have been reported.

In this work, we modified nanocrystalline ZSM-5 zeolite by TPAOH treatment and investigated its catalytic performance in MTG reaction and its physical and chemical properties.

2. Experimental

2.1. Catalyst preparation

Nanocrystalline NaZSM-5 zeolite powder ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 26, crystal size 70–100 nm), synthesized using the patented method [14], was treated with 0.1 mol/L TPAOH solution for 24, 48, or 72 h at 170 °C in an autoclave, followed by washing with deionized water and filtering. After drying and calcination, the samples were ion exchanged three times with 0.4 mol/L NH_4NO_3 solution for 2 h at 75 °C, followed by washing, filtering, drying at 100 °C, and calcination in static air at 540 °C for 4 h. The obtained TPAOH-treated nanocrystalline

HZSM-5 samples were designated HZ (no treatment), T24-HZ (treated for 24 h), T48-HZ (treated for 48 h), and T72-HZ (treated for 72 h). Strips of the TPAOH-treated nanocrystalline HZSM-5 samples were obtained by extruding mixtures of the TPAOH-treated nanocrystalline HZSM-5 samples with alumina (weight ratio of HZSM-5: Al_2O_3 = 4:1), followed by washing, drying at 100 °C, and calcination in static air at 540 °C for 4 h. The obtained samples were designated nHZ, T24, T48, and T72.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2400 diffractometer at a scanning rate of 6°/min from 5° to 50°. The crystal sizes and morphologies of the samples were examined using scanning electron microscopy (SEM; JEOL JSM-5600 LV). ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded using a Bruker Avance III 600 spectrometer. ^{27}Al MAS NMR spectra were recorded at a resonance frequency of 156.4 MHz with a spinning rate of 12 kHz, using a 0.75 μs ($\pi/8$) pulse with a 2 s recycle delay; chemical shifts were referenced to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt. ^{29}Si MAS NMR spectra were recorded at a resonance frequency of 119.2 MHz with a spinning rate of 8 kHz, using a 4 μs ($\pi/2$) pulse with a 2 s recycle delay; chemical shifts were referenced to $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. X-ray photoelectron spectroscopy (XPS) was performed using a VG K-Alpha photoelectron spectrometer using $\text{Al } K_{\alpha}$ radiation. Surface area and pore size distribution were obtained with a Quantachrome AUTOSORB-1 analyzer using low-temperature N_2 adsorption. The adsorption capacities of *n*-hexane and cyclohexane were measured at 25 °C using a flow adsorption method. The acidic properties of the samples were obtained with a Quantachrome CHEMBET 3000 instrument using the NH_3 temperature-programmed desorption (TPD) method.

2.3. Catalytic tests

The prepared catalysts were tested for MTG in a continuous-flow fixed-bed reactor at atmospheric pressure. The HZSM-5 catalyst (1.0 g, 20–40 mesh) was placed in the center of the stainless-steel tubular reactor and $\gamma\text{-Al}_2\text{O}_3$ (1.0 g) was placed above it, separated by a layer of alumina balls. The weight hourly space velocity was 2.0 h^{-1} , and the reaction temperature was 380 °C. The effluent from the reactor was separated into gaseous and liquid products using ice-water.

Analysis of the gaseous products was performed using a Tianmei GC 7890F gas chromatograph equipped with an HP-PLOTQ capillary column (30 m $\times$ 4 mm), and the organic phase of the liquid product was analyzed using the GC 7890F gas chromatograph equipped with an OV-101 capillary column (50 m $\times$ 0.23 mm $\times$ 0.50 μm), with quantitative analysis using PONA software. The conversion of methanol to hydrocarbon products (dimethyl ether (DME) was considered to be reactant), X_M , is defined as $X_M = (1 - \text{the molar percentage of methanol in the effluent}/\text{the molar percentage of methanol in the reactant}) \times 100\%$.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the XRD patterns of the HZSM-5 samples. The number of peaks and the peak positions did not change after TPAOH treatment. The peak intensities at both low ($2\theta = 7.8^\circ$ and 8.7°) and high ($2\theta = 22.9^\circ$, 23.6° , and 24.3°) diffraction angles increased slightly. This indicates that the TPAOH treatment did not adversely affect the crystal structure, and the relative crystallinities of the modified samples increased slightly, probably as a result of changes in an unstable phase. Li et al. [15] modified a ZSM-5 zeolite in a mixed alkaline aqueous solution of TPAOH and an inorganic base, NaOH, and found that the relative crystallinity of the zeolite increased with increasing TPA^+/OH^- ratio, indicating that the TPAOH modification is controllable.

Figure 2 shows SEM images of the HZSM-5 samples before extrusion. It can be seen that the crystal morphology was more regular and the crystals were larger after TPAOH treatment. These results are contrary to some published papers [6,7,9,10], which reported that the zeolite angles disappeared, the edges blurred, and the surfaces became rougher after NaOH treatment. These results are also different from those in another report [15], which showed that the zeolite surface became rougher with the increasing TPA^+/OH^- ratio after treatment with a mixed alkaline aqueous solution of TPAOH and NaOH. This shows that the inorganic base, NaOH, had a particularly strong influence on the zeolite, whereas the organic alkaline TPAOH had a more moderate influence and stabilized the zeolite structure. The TPAOH solution acts as a lye and can lead to the removal of framework silicon as well as framework aluminum. Also, acting as a template, the TPAOH solution may lead to secondary crystallization of amorphous species, non-framework silicon, and non-framework aluminum on the zeolite surface. Consequently, the relative crystallinity of the sample increased and the crystal size increased after TPAOH treatment. Huang [16] observed secondary crystallization when TS-1 was treated with TPAOH solution, and the crystal grains became more regular and some new crystal grains appeared after modification.

Fig. 1. XRD patterns of HZSM-5 with different TPAOH treatment time. (1) nHZ; (2) T24; (3) T48; (4) T72.

Fig. 2. SEM images of HZSM-5 with different TPAOH treatment time before extrusion. (a) HZ; (b) T24-HZ; (c) T48-HZ; (d) T72-HZ.

Figure 3(a) shows the ^{27}Al MAS NMR spectra of the HZSM-5 samples before extrusion. The spectra of all the samples are characterized by an intense and sharp signal at $\delta = 54$, and a weaker and broad signal at $\delta = 0$, arising from tetrahedrally coordinated framework aluminum and six-coordinated non-framework aluminum, respectively. For the HZ sample, there is a signal at $\delta = 37$ attributed to five-coordinated framework aluminum. For the T24-HZ sample, the signal from five-coordinated framework aluminum decreases significantly, and the signal from non-framework aluminum increases significantly, clearly indicating removal of aluminum from the

Fig. 3. ^{27}Al (a) and ^{29}Si (b) MAS NMR spectra of HZSM-5 with different TPAOH treatment time before extrusion. (1) HZ; (2) T24-HZ; (3) T48-HZ; (4) T72-HZ.

lattice. For the T48-HZ sample, the signal from non-framework aluminum increases further, showing that removal of aluminum from the lattice continues to occur. For the T72-HZ sample, the signal from non-framework aluminum decreases significantly, indicating the end of dealumination and the conversion of non-framework aluminum to framework aluminum.

Figure 3(b) shows the ^{29}Si MAS NMR spectra of the samples before extrusion. All the samples have signals at $\delta = -113$ and -106 , attributed to framework $\text{Si}(\text{OSi})_4$ (Q4) and $\text{Si}(\text{OSi})_3(\text{OAl})$ (Si1Al), respectively. For the T24-HZ sample, the framework Si/Al ratio increases from 20.8 to 30.8 compared with the HZ sample as a result of removal of framework aluminum, in agreement with the ^{27}Al MAS NMR spectra. For the T48-HZ sample, the framework Si/Al ratio further increases to 40.4, showing that removal of aluminum from the lattice is still occurring. For the T72-HZ sample, the framework Si/Al ratio changes little compared with the T48-HZ sample, increasing from 40.4 to 41.7. Based on a combination of these results and the ^{27}Al MAS NMR spectra, it can be concluded that secondary crystallization of the zeolite occurs when the TPAOH treatment time is longer than 48 h, resulting in migration of non-framework aluminum and non-framework silicon to the zeolite surface and their transformation into framework species. Analysis of the framework Si/Al ratio shows that the migration rate of non-framework silicon is faster than that of non-framework aluminum, especially in the treatment stage from 24 to 48 h.

Figure 4 shows the Si 2p and Al 2p XPS spectra of the HZSM-5 samples before extrusion. The surface Si/Al ratios of the samples obtained from the XPS spectra are shown in Table 1. For the HZ sample, the surface Si/Al ratio is 8.23; it is 13.2 for the T24-HZ sample, reaches a maximum, 17.9, for the T48-HZ sample, and decreases to 10.4 for the T72-HZ sample. The XPS spectra show that secondary crystallization of the zeolite does occur, making non-framework silicon migrate to the zeolite surface, resulting in an increase in the amount of framework silicon on the zeolite surface. Simultaneously, with increasing treatment time, some of the non-framework aluminum will migrate to the zeolite surface, and this is the reason for the decrease in the surface Si/Al ratio for the T72-HZ sample. Also, the results show that the migration of non-framework silicon is much easier, and the migration rate is faster, than those of non-framework aluminum during secondary crystallization, in

Table 1

Surface Si/Al ratios of HZSM-5 with different TPAOH treatment time before extrusion.

Sample	Surface Si/Al
HZ	8.2
T24-HZ	13.2
T48-HZ	17.9
T72-HZ	10.4

agreement with the ^{27}Al and ^{29}Si MAS NMR results.

The pore properties of the HZSM-5 samples are shown in Table 2. The Brunauer-Emmett-Teller (BET) surface areas, micropore areas, micropore volumes, and total pore volumes of the samples all increase after TPAOH treatment, especially the micropore areas. The N_2 adsorption-desorption isotherms are shown in Fig. 5. The hysteresis loops in the isotherms of the modified samples are more pronounced and migrate upwards. These results are similar to those in some previous publications [5–9], which reported that these features were attributed to desilication and formation of new mesopores in ZSM-5 zeolite treated with NaOH solution. Compared with NaOH-treated samples, the changes in the hysteresis loops of the TPAOH-treated samples are less obvious, which may be the result of the moderate degree of modification caused by the TPAOH treatment, rather than new mesopore formation. However, TPAOH treatment can lead to an increase in the micropore volume, as shown by the data in Table 2. The increase in the BET surface area is mainly caused by dissolution of framework species [5,6]. The micropore area increase is possibly attributable to desilication, dealumination, and secondary crystallization of the zeolite during TPAOH treatment, resulting in amorphous species becoming framework species, and clearing of the channels.

Table 2

Pore properties of HZSM-5 with different TPAOH treatment time.

Sample	A_{BET} (m^2/g)	A_{ext}^a (m^2/g)	A_{micro}^a (m^2/g)	V_{micro}^a (ml/g)	V_{total}^b (ml/g)
nHZ	345	146	199	0.09	0.30
T24	373	141	232	0.10	0.31
T48	377	142	234	0.10	0.31
T72	373	147	226	0.10	0.31

^a t -Method. ^b Volume adsorbed at $p/p_0 = 0.99$.

Fig. 4. Si 2p and Al 2p XPS spectra of HZSM-5 with different TPAOH treatment time before extrusion. (a) HZ; (b) T24-HZ; (c) T48-HZ; (d) T72-HZ.

Fig. 5. N_2 adsorption-desorption isotherms of HZSM-5 with different TPAOH treatment time. (a) nHZ; (b) T24; (c) T48; (d) T72.

Figure 6 shows the adsorption curves of *n*-hexane and cyclohexane on the nHZ and T72 samples. The adsorption rates and capacities of both *n*-hexane and cyclohexane on the T72 sample are higher than those on nHZ. It can be concluded that the TPAOH treatment clears the channels of the HZSM-5 zeolite and increases the pore volume; this is consistent with the N_2 adsorption-desorption analysis.

Figure 7 shows the NH_3 -TPD curves of the HZSM-5 samples. The high-temperature peak arises from strong acid sites and the occurrence of the low-temperature peak is related to the interaction of ammonia with different weak acid sites. It can be seen that the area of the low-temperature peak decreases, whereas that of the high-temperature peak increases, after TPAOH treatment, indicating a reduction in the number of weak acid sites and an increase in the number of strong acid sites. The number of weak acid sites increases with increasing TPAOH treatment time, whereas the number of strong acid

sites first decreases and then increases. The two NH_3 desorption peaks shift towards lower temperatures after TPAOH treatment, showing a reduction in the strengths of the strong and weak acids. The TPAOH treatment time has less effect on the reduction in the acid strength. The change in acidity is caused by aluminum redistribution in the HZSM-5 zeolite, which may be attributed to desilication, dealumination, and secondary crystallization of the zeolite during TPAOH treatment. Presumably, the Al_2O_3 mixed with the nanocrystalline HZSM-5 during extrusion has an impact on the acidity of the HZSM-5 zeolite, leading to conversion from non-framework aluminum to framework aluminum during high-temperature calcination. However, further verification is needed.

3.2. Catalytic testing

Figure 8 shows the conversion of methanol to hydrocarbons as a function of time on stream for the four catalyst samples. The parent nHZ sample displays an activity above 98% within 70 h, and deactivation is rather fast, with the activity falling below 90% after 75 h on stream. The lifetime of the T24 sample is significantly better, as the conversion remains above 98% for 170 h, and deactivation is rather slow, with the activity falling below 90% after 200 h on stream. These effects are more pronounced for the T48 and T72 samples, i.e., the activity of the T48 sample falls below 90% after 210 h and the activity of the T72 sample falls below 90% after 230 h. It is concluded that the

Fig. 6. Adsorption capacities of HZSM-5 before and after treatment with TPAOH for *n*-hexane(a) and cyclohexane(b).

Fig. 7. NH_3 -TPD profiles of HZSM-5 with different TPAOH treatment time. (1) nHZ; (2) T24; (3) T48; (4) T72.

Fig. 8. Conversion of methanol/DME to hydrocarbons as a function of time on stream. (1) nHZ; (2) T24; (3) T48; (4) T72.

stability of the catalyst is significantly improved as a consequence of modification, and the lifetime of the catalyst increases with increasing TPAOH treatment time.

These results, in combination with the results of sample characterization, show that TPAOH treatment not only increases the BET surface area and exposes many more catalytic activity sites, improving adsorption and activation of reactant molecules, but also increases the micropore volume, clears the channels, and improves the diffusion capacity and coke tolerance; these are the reasons for the increased stabilities of the modified samples.

To obtain a more quantitative and precise measurement of the improvement in catalytic performance, the loosely defined concept of catalyst lifetime will be supplemented by the total conversion capacities. Based on Bjørgen's work [5], this is done by plotting the methanol conversion against the number of grams of methanol converted per gram of catalyst, and extrapolating to zero conversion, thus obtaining a value for the total capacity of the catalyst for MTG conversion until complete loss of activity; this is shown in Fig. 9. For the nHZ sample, the conversion capacity is 260 g(methanol)/g(catalyst). For the T24, T48, and T72 samples, the conversion capacities are 635, 680, and 750 g/g, respectively. The conversion capacity therefore

Fig. 9. Conversion of methanol plotted against the cumulative amount of methanol converted to hydrocarbons. Extrapolation to zero conversion gives the total conversion capacities of the four samples. (1) nHZ; (2) T24; (3) T48; (4) T72.

Table 3
Gaseous product distribution.

Sample	Product distribution (mol%)								C ₃ H ₆ /C ₂ H ₄
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅	
nHZ	7.6	11.5	6.1	8.6	9.7	26.0	6.0	13.9	0.8
T24	6.7	8.7	6.6	8.1	11.1	28.2	6.6	15.3	0.9
T48	6.7	9.1	6.8	8.4	10.2	27.7	6.8	15.5	0.9
T72	6.6	9.0	7.0	8.2	11.5	28.5	6.8	14.8	0.9

increases by a factor of about 3 as a result of the most severe treatment. In industry, catalytic reactions are seldom allowed to run until complete deactivation, but the calculated values show that the catalytic performance has been significantly improved by the TPAOH treatment.

Table 3 shows the gaseous product distribution, mainly light olefins and alkanes. Obviously, compared with the parent nHZ sample, the modified samples have less methane, more propane, and an increased propene/ethylene ratio in the gaseous products. Methane comes from the demethylation of aromatics and carbon precursors [17], so the more serious the carbon deposition, the more demethylation occurs, and the higher the methane formation. Some researchers have used the change in methane content as an indicator for measuring catalyst deactivation, i.e., a reduction in the methane content shows a slowing of the carbon deposition rate. We hypothesize that the diffusion of reactant and product molecules increases because the TPAOH treatment clears the channels of the HZSM-5 zeolite. Carbenium ions from propylene react with high olefins to give propane and dienes or aromatic compounds [18], as a result of hydrogen transfer reactions. The higher the propane content, the faster the hydrogen transfer reactions [19]. Hydrogen transfer is a bimolecular reaction, so it needs two acid sites with suitable and similar acid strengths. Some researchers [20] therefore consider that hydrogen transfer reactions may occur if the catalyst has a suitable space structure and active sites. After TPAOH treatment, the BET surface area and number of active sites increase, and the channels of HZSM-5 zeolite are cleared; these effects are beneficial to hydrogen transfer reactions between hydrocarbon molecules. The increase in the propene/ethane ratio is mainly caused by a decline in the ethane content, as reported by Bjørgen et al. [5], caused mainly by a decline in the rate of ethane formation via the aromatic-based hydrocarbon pool mechanism. As stated above, as the diffusivity increases and the time for which each aromatic molecule resides in the micropores is shortened, as a result of clearing the channels after TPAOH treatment, the probability of undergoing the reaction steps required for ethane formation diminishes.

Table 4 shows the liquid product distribution, mainly C₅–C₁₀

Table 4
Liquid product distribution.

Sample	Product distribution (vol%)				
	<i>i</i> -Paraffins	<i>n</i> -Paraffins	Olefins	Aromatics	Durene
nHZ ^a	31.3	4.1	9.7	51.7	4.0
T24 ^b	33.5	3.9	8.4	50.2	5.3
T48 ^b	34.4	3.2	7.8	50.8	4.3
T72 ^b	33.1	3.5	7.6	51.5	4.3

^aThe mean value of 70 h. ^bThe mean value of 170 h.

long-chain isoparaffins, olefins, and aromatics. Compared with the parent nHZ sample, the modified samples give more isoparaffins, less olefins, and a similar amount of aromatics. The main MTG reactions are as follows [21]: (1) generation of C₂–C₃ light olefins [22]; (2) generation of C₄–C₆ mixed olefins (the majority are isoolefins) via alkylation of C₂–C₃ light olefins and oligomerization reactions between C₂–C₃ light olefins and other olefins; (3) generation of aromatics via dehydrocyclization of C₆–C₁₀ oligomers formed by oligomerization of linear C₂–C₅ olefins; (4) further isomerization and alkylation reactions of aromatics; and (5) hydrogen transfer reactions of isoolefins, which are not prone to oligomerization, to isoparaffins.

The main reason for the increase in the amount of isoparaffins and the decrease in the amount of olefins may be acceleration of the hydrogen transfer reactions. As mentioned above, TPAOH treatment improves the space structure and acidity of the samples, which strengthens the hydrogen transfer reaction activity. It can be seen from step (3) that aromatics are manufactured through polymerization and cyclization of light olefins, and this is associated with the pore structure and the number of strong acid sites in the zeolite. It has been reported that the generation of aromatics in MTG needs strong acidity [23,24]. As indicated by the NH₃-TPD results, TPAOH treatment increases the number of strong acid sites but reduces the strong acid strength. So, there is little change in the amount of aromatics. Moreover, more durene is seen for the modified samples, which is commonly attributed to the cleared channels assisting generation and diffusion of large molecules.

4. Conclusions

The physical and chemical properties of a nanocrystalline ZSM-5 zeolite modified with TPAOH solution were studied; the catalytic performance of the modified zeolite in MTG reaction was also investigated. The modification led to desilication, dealumination, and secondary crystallization of the zeolite,

resulting in the migration of non-framework silicon and non-framework aluminum to the zeolite surface. The structures of the modified samples were basically unchanged, but the relative crystallinities increased and the crystal morphologies were more regular. The redistribution of framework silicon and framework aluminum caused an increase in the surface Si/Al ratio and the BET surface area, and the exposure of increased numbers of catalytic activity sites. The diffusion capacity and coke tolerance improved, which was attributed to an increase in the micropore volume and clearing of the channels. The stability of the catalyst was significantly improved, and the total conversion capacity increased by a factor of 3 as a consequence of the most severe treatment. Hydrogen transfer reactions became faster and led to more isoparaffins and less olefins in the liquid products.

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Graphical Abstract

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Modification of nanocrystalline HZSM-5 zeolite with tetrapropylammonium hydroxide and its catalytic performance in methanol to gasoline reaction

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Tetrapropylammonium hydroxide treatment of the HZSM-5 zeolite improved the diffusion capacity and coke tolerance through desilication, dealumination, and secondary crystallization, reflected by the significantly increased catalyst lifetime.

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四丙基氢氧化铵改性纳米HZSM-5分子筛及其在甲醇制汽油中的催化性能

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摘要: 采用四丙基氢氧化铵(TPAOH)溶液对纳米ZSM-5分子筛进行改性, 运用X射线衍射、扫描电镜、²⁷Al和²⁹Si固体核磁、X射线光电子能谱、N₂物理吸附脱附法和NH₃程序升温脱附等手段对所制样品进行了表征, 并评价了其催化甲醇制汽油反应性能. 结果表明, 改性后的HZSM-5相对结晶度增加, 晶体形貌更加规整, 表面硅铝比增加, 比表面积和微孔表面积增大, 强酸位酸量增多. 同时, TPAOH改性不仅可以使分子筛脱硅脱铝, 而且伴有二次晶化补硅补铝, 改变了分子筛的硅铝分布. 改性的HZSM-5在甲醇制汽油反应中的稳定性大幅度提高, 其寿命由70 h增至170 h以上, 随着TPAOH处理时间的增加, 催化剂寿命增加, 氢转移反应加快, 导致油相产品中异构烷烃增多, 烯烃减少.

关键词: 纳米HZSM-5; 分子筛; 四丙基氢氧化铵; 甲醇制汽油

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1. 前言

甲醇制汽油(MTG)工艺^[1~3]由Mobil公司于1976年开发, 它主要以煤或天然气作原料, 经合成气制甲醇, 再将粗甲醇转化为高辛烷值高品质汽油. 随着世界石油资源的日益匮乏和国内甲醇产能的日益过剩, 甲醇作为新的化石原料来源已成为一种趋势; 而且由甲醇制得的汽油不含硫和氯等组分, 抗爆震性好.

ZSM-5分子筛是MTG技术的关键, 其骨架中含有两种相互交叉的孔道体系: 椭圆形十元环直孔道和圆形之字形弯曲孔道, 其孔径分别约为0.51 nm × 0.55 nm和0.53 nm × 0.56 nm. 因此, ZSM-5能使汽油沸点范围内的烃分子通过, 而临界尺寸大于均四甲苯的分子很难通过, 使MTG反应选择性较高. 但由于母体HZSM-5的酸性强, 反应过程中极易发生积炭失活^[4], 需要对其改性以制得性能更加优良的催化剂.

近年来, 碱改性法备受关注, 即选择性地从分子筛

骨架上脱去硅原子, 从而引入介孔或大孔, 使得分子筛的扩散能力和催化裂化能力增加. Bjørgen等^[5]发现, 经NaOH改性的ZSM-5分子筛比表面积增加, 骨架Si/Al比降低, 有中孔产生, 稳定性增加, 催化MTG反应可生成更多的芳烃和烷烃. Ogura等^[6]和Suzuki等^[7]使用NaOH处理具有MFI结构的ZSM-5分子筛, 发现处理后样品的吸附曲线和孔分布发生变化, 其催化活性明显提高. Groen等^[8,9]采用碱处理选择性地从分子筛骨架中脱除Si元素, 致使分子筛结构改变. Ni等^[10]采用NaOH对ZSM-5分子筛进行处理, 使分子筛产生中孔, 配合Zn浸渍改性, 在MTG反应中可以显著提高催化剂的稳定性和液态烃的收率. 肖强等^[11]采用NaOH处理含有模板剂的丝光沸石, 发现其催化异丁烯的转化率提高了13%. 比较而言, 有机碱改性的速率较温和且具有可控性, 目前多用于TS-1分子筛的改性. 毛璟博等^[12]采用四丙基氢氧化铵(TPAOH)对微米TS-1进行改性, 发现改性后的TS-1基本结构没有明显变化, 但在内部出现蚀刻现象,

其催化苯酚羟基化和丁酮氨氧化性能明显提高。夏丽贞^[13]采用TPAOH等有机碱对纳米TS-1进行改性,发现改性后催化剂在甲乙酮氨氧化反应中的重复使用性能显著提高。目前,采用有机碱处理ZSM-5分子筛还鲜见报道。本文使用TPAOH溶液对纳米ZSM-5分子筛进行改性,考察了处理时间对HZSM-5分子筛的物化性质及其催化MTG反应性能的影响。

2. 实验部分

2.1. 催化剂的制备

按照专利^[14]方法合成纳米NaZSM-5分子筛($\text{SiO}_2/\text{Al}_2\text{O}_3$ 摩尔比为26, 70~100 nm),再将其与TPAOH溶液(0.1 mol/L)混合,置于高压釜中,在170 °C下分别处理24, 48和72 h,经过滤、烘干和540 °C焙烧后,得到改性的钠型ZSM-5分子筛样品。将未处理的纳米ZSM-5或改性后的钠型分子筛放入硝酸铵水溶液(0.4 mol/L)中,按固液比1:10在75 °C下交换3次,每次2 h,用去离子水洗涤至中性,抽滤,在100 °C烘干,540 °C焙烧4 h,制得TPAOH改性的氢型纳米ZSM-5分子筛样品,分别记为HZ(未处理), T24-HZ(处理24 h), T48-HZ(处理48 h)和T72-HZ(处理72 h)。将氢型分子筛与拟薄水铝石混合(干基质量比为4:1),加入适量田菁粉,再加入稀硝酸溶液(体积分数10%),搅拌混合均匀,挤条成型,室温阴干,于100 °C烘干,540 °C焙烧4 h,得到TPAOH改性纳米HZSM-5分子筛样品,分别记为nHZ, T24, T48和T72。

2.2. 催化剂的表征

X射线衍射(XRD)表征在日本Rigaku公司D/max-2400型X射线粉末衍射仪上进行, $\text{Cu K}\alpha$ 辐射,扫描范围 $2\theta = 5^\circ \sim 50^\circ$,扫描步幅 0.02° 。催化剂形貌在日本JEOL公司JSM-5600 LV型扫描电子显微镜(SEM)上观测,电压20 kV。 ^{27}Al 和 ^{29}Si 固体核磁(MAS NMR)谱在Bruker Avance III 600型核磁共振波谱仪上测量,使用4 mm MAS探头。 ^{27}Al MAS NMR谱的化学位移以三甲基硅丙磺酸钠(DSS)为外标,共振频率156.4 MHz,样品转速12 kHz,脉冲宽度 $0.75 \mu\text{s} (\pi/8)$,采样延迟2 s; ^{29}Si MAS NMR谱的化学位移以 $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ 为外标,共振频率119.2 MHz,样品转速8 kHz,脉冲宽度 $4 \mu\text{s} (\pi/2)$,采样延迟4 s。X射线光电子能谱(XPS)分析采用英国VG公司K-Alpha型X射线光电子能谱仪测定,激发源为 $\text{Al K}\alpha$ 。 N_2 物理吸附脱附实验使用美国Quantachrome公司AUTOSORB-1型物理吸附仪,测试前先在350 °C抽真空,孔分布及孔体积由H-K方程计算得到,比表面积由

BET方法求得。以正己烷和环己烷为吸附质,在25 °C采用连续流动法测定样品的吸附量。 NH_3 程序升温脱附(NH_3 -TPD)表征在美国Quantachrome公司CHEMBET 3000型化学吸附分析仪上进行,He为载气,升温速率10 °C/min。

2.3. 催化剂的评价

MTG反应在连续流动常压固定床上进行,将1 g HZSM-5样品(20~40目)置入长40 cm、内径0.8 cm的不锈钢管式反应器中部(恒温段),填充一层惰性瓷球,再置入1 g的 $\gamma\text{-Al}_2\text{O}_3$ 催化剂,反应器其它非恒温段填充惰性瓷球,液体原料甲醇由双柱塞泵连续注入反应器,甲醇重时空速为 2.0 h^{-1} ,反应温度为380 °C。产物经冰水气液分离,液相产物又经分液漏斗分为水相和油相,气相产物分析采用天美GC 7890F型气相色谱仪,HP-PLOTQ毛细柱(30 m $\times$ 4 mm),FID检测器;油相产物分析采用天美GC 7890F型气相色谱仪,OV-101毛细管柱(50 m $\times$ 0.23 mm $\times$ 0.50 μm),FID检测器,色谱数据用石科院PONA软件分析计算,得到产物的芳烃、烯烃、正构烷烃、异构烷烃及环烷烃的体积含量。甲醇转化率(二甲醚和甲醇一起被认为是反应物) X_M 计算式为: $X_M = (1 - \text{反应产物中甲醇的摩尔分数} / \text{反应进料中甲醇的摩尔分数}) \times 100\%$ 。

3. 结果与讨论

3.1. HZSM-5分子筛的表征

图1为改性前后HZSM-5的XRD谱。可以看出,改性后的样品在 $2\theta = 7.8^\circ, 8.7^\circ, 22.9^\circ, 23.6^\circ$ 和 24.3° 处均有特征峰出现,且衍射峰相对强度均有所增加,说明TPAOH处理并未破坏ZSM-5的MFI晶体结构,而可能使其中一些不稳定相发生了转变,导致相对结晶度有所增加。李莎等^[15]采用TPAOH/NaOH混合碱体系对ZSM-5进行改性,发现随着 TPA^+/OH^- 的增大,分子筛的相对结晶度逐渐增加,说明TPAOH对分子筛具有可调控性。

图2为改性前后HZSM-5的SEM照片。可以看出,经TPAOH处理后的HZSM-5晶粒形貌更加规整,并且颗粒有增大趋势。但文献报道^[6,7,9,10],经NaOH溶液处理过的分子筛棱角消失,边缘模糊,表面粗糙,与本文结果不同,也与采用TPAOH/NaOH混合碱体系处理ZSM-5不尽相同,但是李莎等^[15]发现,随着 TPA^+/OH^- 比值减小,分子筛表面的粗糙程度加剧,说明无机碱NaOH对分子筛的作用较强,有机碱TPAOH的作用较温和,且对分子筛结构的稳定化能力较强。TPAOH处理后的分子筛

晶粒增大且变得规整,可能是由于TPAOH作为碱液,在处理过程中,使分子筛中的骨架硅物种脱除,同时也使得部分铝物种脱除;但TPAOH又是一种模板剂,因此脱除下来的硅物种和铝物种以及原来表面的无定形物种还会在分子筛表面发生二次晶化,致使晶粒增大且更加规整.黄先亮^[16]也发现,采用有机碱TPAOH对TS-1进行处理,会发生二次晶化过程,晶粒结构变得完整且会出现新的晶粒.

图3为改性前后HZSM-5的²⁷Al和²⁹Si MAS NMR谱.由图3(a)可见,样品在 $\delta = 54$ 有一个尖锐而强的峰,在 $\delta = 0$ 附近有一个宽而较弱的峰,分别归属于分子筛的四配位骨架铝和六配位非骨架铝.对于未处理的HZSM-5样品,在 $\delta = 37$ 还有较明显的信号峰,归属于五配位的骨架铝.经过TPAOH处理24 h后的样品,五配位骨架铝信号峰的相对强度明显降低,但非骨架铝信号峰的明显增加,表明经过TPAOH处理后, HZSM-5样品发生了较明显的脱铝.随着处理时间增加到48 h,非骨架铝信号峰相对强度进一步增加,表明脱铝过程继续发生;至72 h,非骨架铝信号峰相对强度反而明显降低,这预示着脱铝过程结束,同时部分非骨架铝有可能向骨架铝发生了转变.如图3(b)所示,所有样品的²⁹Si MAS NMR谱均在 $\delta = -113$ 和 -106 处出现共振峰,分别归属于分子筛骨架Si(OSi)₄ (Q4)和Si(OSi)₃(OAl) (Si1Al).经过TPAOH处理24 h,由硅谱计算样品的骨架Si/Al比从20.8增至30.8,说明有骨架铝脱除,与²⁷Al MAS NMR谱结果一致.随着处理时间增大到48 h, Si/Al比进一步增加到40.4,说明脱铝仍较明显;至72 h, Si/Al比略增至41.7.结合²⁷Al MAS NMR结果可认为,48 h后脱铝过程结束,同时可能伴有二次晶化过程,脱除下来的非骨架硅和非骨架铝可以重新迁移到分子筛骨架.基于骨架Si/Al比持续增加可以看出,二次晶化过程中脱除下来的硅迁移到分子筛骨架的速度快于非骨架铝迁移到分子筛骨架的,特别是在24~48 h的处理阶段.

采用XPS表征可得到分子筛表面上Si 2p和Al 2p的XPS谱峰面积,结果见图4.由此算得的分子筛表面Si/Al比示于表1.可以看出, HZSM-5表面硅铝比为8.23,经TPAOH处理后升高,至48 h达最高,然后又降低.结果表明, TPAOH处理过程中确可发生二次晶化,使得脱除下来的硅迁移到分子筛外表面,导致表面硅含量增加.随着处理时间的延长,脱除下来的少量非骨架铝也迁移到分子筛表面,因此表面Si/Al比呈现下降趋势.这也进一步说明了二次晶化过程中非骨架硅较易发生迁

移,并且迁移速度快于非骨架铝,与²⁷Al和²⁹Si MAS NMR结果一致.

表2为各分子筛样品的孔结构性质.可以看出, TPAOH处理以后的分子筛比表面积、微孔表面积、微孔体积和总孔体积均有所增加,特别是微孔表面积.

图5为TPAOH改性前后分子筛样品的N₂吸附-脱附等温线.由图可见,改性后HZSM-5的滞后环稍有增大,并且向上迁移,与文献[5~9]中采用NaOH处理ZSM-5的结果类似,可认为是分子筛骨架脱硅和产生新的介孔所致.而TPAOH处理后分子筛滞后环的变化不太显著,可能是由于TPAOH处理比较温和,未能产生较为明显的介孔,但仍能说明改性后的HZSM-5微孔体积有所增加,与表2结果一致.比表面积的增加主要是由于骨架物种的脱除^[5,6];微孔体积的略有增加是由于骨架脱硅脱铝所致,还可能是因为原本孔道内的无定形物种在二次晶化过程中转化为了骨架物种,疏通了分子筛的孔道.

图6为nHZ和T72的正己烷和环己烷的吸附曲线.经过TPAOH处理72 h以后, HZSM-5的正己烷和环己烷的吸附量和吸附速率均增加,说明TPAOH处理疏通了分子筛的孔道,使分子筛孔体积变大.这与N₂物理吸附分析结果一致.

图7为改性前后HZSM-5的NH₃-TPD曲线.图中低温和高温NH₃脱附峰分别对应于催化剂表面的弱酸位和强酸位.可以看出,经TPAOH处理后, HZSM-5分子筛的低温脱附峰面积减小,高温脱附峰面积增大,表明弱酸位的酸量降低,强酸位的酸量增加.另外,随着TPAOH处理时间的延长,弱酸位的酸量增加,强酸位的酸量先减少后增加.经TPAOH处理后,样品的两个NH₃脱附峰的温度均向低温方向移动,说明分子筛的强酸位和弱酸位的酸强度都有所减弱,但是处理时间对样品酸强度的影响不大. TPAOH处理过程中,分子筛发生脱硅脱铝,并且伴随二次晶化, Al在HZSM-5分子筛上发生重新分布,导致酸量和酸强度的不同变化.另外,由于分子筛挤条成型过程中加入了拟薄水铝石,焙烧过程中可能有部分铝物种进入骨架,对分子筛的酸性产生影响,但还需进一步验证.

3.2. HZSM-5在MTG反应中的催化性能

图8是改性前后HZSM-5分子筛上MTG反应的甲醇转化率随时间的变化.由图可见,在反应70 h内, nHZ样品上甲醇转化率保持在98%以上,随后迅速下降,而经过TPAOH处理的HZSM-5上98%以上的甲醇转化率能保

持170 h, 然后才慢慢下降; T24在反应200 h后, 甲醇转化率降到90%以下, 与母体相比, 催化剂的稳定性得到极大改善. 此外, T48在反应约210 h, 甲醇转化率降到90%以下, T72在反应约230 h降到90%以下, 可知, 随着TPAOH处理时间的增加, 催化剂寿命延长.

结合上文表征可知, TPAOH处理增加了分子筛的比表面积, 更多催化活性位的暴露有利于原料分子的吸附和活化; 微孔体积增加, 孔道疏通, 减小了分子的扩散阻力, 提高了催化剂的扩散能力和容炭能力. 这是催化剂稳定性随着TPAOH处理时间的增加而增加的原因.

为了定量改性前后HZSM-5催化性能的改善情况, 可根据甲醇转化率随时间变化的趋势图推算甲醇转化率随着已转化甲醇质量的变化趋势^[5], 结果见图9. 由此图可得到催化剂完全失活前, 即甲醇转化率为零之前已经转化的甲醇质量, 以此来定量反映催化剂的催化能力. 对于nHZ, 甲醇转化能力约为260 g (甲醇)/g (催化剂), T24的约为635 g/g, T48和T72的分别约为680和750 g/g. 可见, 经TPAOH处理72 h, 所得样品催化甲醇转化能力可提高到原来的3倍. 虽然工业应用中很少有直到催化剂完全失活才停止反应的情况, 但是这种推算仍然能说明经TPAOH改性后催化剂催化能力得到了显著改善.

各样品上MTG反应的气相产物含量列于表3. 可以看出, 经TPAOH处理后, 所得样品上气相产物较为明显的变化是甲烷减少, 丙烷增多, 丙烯/乙烯比增加, 但处理时间的影响不明显. 甲烷主要是由芳烃和积炭前驱体通过脱甲基反应生成^[17], 催化剂的积炭程度越严重, 脱甲基反应越明显, 生成的甲烷越多. 人们常用甲烷含量的变化来反映催化剂的失活情况, 气相产物中甲烷含量减少, 说明积炭速率降低. 这是因为TPAOH改性疏通了分子筛的孔道, 有利于反应物和产物分子的扩散; 丙烯生成的碳正离子与高碳烯烃反应得到丙烷和二烯烃或芳烃^[18], 这与氢转移反应相关, 丙烷含量增多, 说明氢转移反应加快^[19]. 氢转移反应是双分子反应, 需要两个酸强度合适且相近的活性中心才能进行, 因此, 有人认为^[20]催化剂必须具有合适的空间结构和活性中心才能发生氢转移反应. 经过TPAOH处理以后, HZSM-5分子筛的比表面积增大, 表面的活性中心增多, 而且分

子筛孔道疏通, 强酸酸量也有所增加, 因而有利于烃分子间的氢转移反应; 丙烯/乙烯比增加主要是由于乙烯的减少所致, 与Björgeren等^[15]的结果一致. 这主要是由于芳烃通过烃池机理生成乙烯的速率降低, 因为TPAOH处理疏通了分子筛的孔道, 使得分子的扩散速率加快, 因此芳烃的停留时间变短, 生成的乙烯减少.

油相产物主要为C₅~C₁₀长链异构烷烃、烯烃和芳烃. 如表4所示, 经TPAOH处理的样品上异构烷烃略有增加, 烯烃略有减少, 芳烃变化不大. MTG主要发生如下反应^[21]: (1)首先生成C₂~C₃低碳烯烃^[22]; (2) C₂~C₃低碳烯烃通过烷基化反应以及与其它烯烃的齐聚反应生成C₄~C₆混合烯烃(大部分为异构烯烃); (3)线性C₂~C₃烯烃齐聚生成C₆~C₁₀齐聚物, 经脱氢环化生成芳烃; (4)芳烃可进一步异构化和烷基化; (5)异构烯烃不易齐聚, 在芳构化反应中可经氢转移生成异构烷烃. 油相催化产品中的异构烷烃略有增加, 烯烃略有减少, 主要原因可能是步骤(5)中的氢转移反应加快, 这与前述的氢转移反应加快原因一致, 说明TPAOH改性调变了分子筛的空间结构和酸分布, 使催化剂的氢转移活性增强. 芳烃主要是通过步骤(3)即低碳烯烃聚合环化生成, 主要与催化剂的孔道结构和强酸中心的量有关. 研究表明, MTG反应中芳烃的生成需要较强的酸性中心^[23,24], 改性后分子筛强酸量稍有增加, 但酸强度有所降低, 因此芳烃变化不大. 另外, 孔道的疏通有利于大分子产物的生成和扩散, 导致产品中均四甲苯的含量增加.

4. 结论

采用TPAOH对纳米ZSM-5分子筛进行改性, 发现处理过程中分子筛会发生脱硅脱铝, 并且伴有二次晶化, 以致非骨架硅铝会重新迁移到分子筛表面, 其中非骨架硅的迁移速度快于非骨架铝. 改性后的HZSM-5相对结晶度增加, 且晶粒形貌更加规整; 骨架硅铝的重新分布导致表面硅铝比增加, 比表面积显著增大, 更多的活性中心暴露出来; 微孔体积增加, 孔道疏通, 使得催化剂的扩散能力和容炭能力提高. 改性后的HZSM-5分子筛在MTG反应中稳定性大幅度增加, 甲醇转化能力提高至原来的3倍, 油相产品中异构烷烃增多, 烯烃减少, 芳烃的量几乎不变.