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Hydrothermal post-synthesis of HZSM-5 zeolite to enhance the coke-resistance of Mo/HZSM-5 catalyst for methane dehydroaromatization

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Hydrothermal post-synthesis was used to modify the micropores and acidity of commercially available HZSM-5 zeolites. The recrystallization and the dynamic incorporation and extraction of the framework Al not only stabilized the framework with high crystallinity, but also inhibited the creation of extra-pores during the post-synthesis in NaOH aqueous solution. The resulted Mo/HZSM-5 catalyst showed rather high catalytic stability and greatly enhanced selectivity towards aromatics for methane dehydroaromatization reaction by effectively inhibiting the coke formation.

KEY WORDS: hydrothermal post-synthesis; HZSM-5 zeolite; methane; dehydroaromatization.

1. Introduction

The catalytic conversion of methane to aromatics and hydrogen is of both scientific importance and industrial interest in the direct utilization of natural gas. Up to now, Mo/HZSM-5 is regarded as the most promising catalyst over which nearly equilibrium conversion of CH_4 to aromatics was achieved with 70–80% selectivity at 973 K [1]. However, It was often observed that the methane conversion decreased drastically with time-on-stream due to the heavy coke formation, which is closely related to the strong acid character of the ZSM-5 zeolite [2–4]. Since only a small concentration of Brönsted acid sites are required to accomplish the oligomerization of the CH_x species formed over Mo to form benzene, several treatments were applied to adjust the distribution of the acidic sites of the ZSM-5 zeolites before and/or after Mo loading [5–8]. Here, we report a novel hydrothermal, post-synthesis treatment of ZSM-5 zeolite in NaOH aqueous solution to create uniform micropores and appropriate acidity. The restructured zeolite catalyst showed significant improvement in catalytic durability and selectivity to aromatics in the methane dehydroaromatization (MDA) reaction.

2. Experimental

2.1. *Hydrothermal post-synthesis treatment of ZSM-5 zeolites and preparation of Mo/ZSM-5 catalysts*

A commercial HZSM-5 with Si/Al mole ratio of 25 was used as the parent zeolite. Five grams of the HZSM-5 zeolite were added to 20 mL 0.04 M NaOH aqueous solution in Teflon-coated stainless steel autoclave. The mixture was gradually heated to 100 °C and kept at this temperature for 12 h, followed by filtration and washing with distilled water. After drying at 100 °C overnight, the solid was calcined at 530 °C for 6 h in air. The sample was then ion-exchanged with 1 M NH_4NO_3 aqueous solution at 60 °C, washed with deionized water, and calcined again at 530 °C for 6 h. The resulting solid was denoted as HZSM-5-S. For comparison, hydrothermal treatment of the parent HZSM-5 with deionized water was also performed with the same procedure and the obtained sample was referred as HZSM-5-H. The Mo/HZSM-5 catalyst (6 wt% Mo loading) was prepared by wet impregnation with an aqueous solution of ammonium heptamolybdate, followed by drying and calcination at 530 °C for 6 h in air.

2.2. *Characterization*

X-ray powder diffraction patterns were recorded on a D/Max-RB powder diffractometer (Rigaku, Japan) with CuK_α radiation. Nitrogen adsorption-desorption isotherms at −196 °C were recorded on a Quantachrome Autosorb-6B gas sorption analyzer after a vacuum pretreatment at 300 °C for 5 h. ^{29}Si and ^{27}Al NWR spectra were recorded at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO_2 rotors. Temperature programmed desorption of ammonia was preformed with AMI-100 instrument. 0.12 grams HZSM-5 samples was heated (10 °C/min) in argon (Ar) to 250 °C and maintained at this temperature for 1 h, and then cooled down to 50 °C

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under Ar flowing. The gas mixture of 10% NH_3/Ar was introduced for 1 h to achieve adsorption equilibrium. Afterward, the sample was purged with Ar at 110 °C for 1 h to remove weakly adsorbed NH_3, and subsequently the temperature was ramped (10 °C/min) to 700 °C. The amount of ammonia in the effluent was monitored online by a thermal conductive detector.

2.3. Catalyst evaluation

Methane aromatization reaction was carried out in a continuous flow, fixed-bed quartz reactor (8 mm i.d.)at 700 °C under atmospheric pressure. 0.2 grams catalysts of 40–60 mesh size were loaded, and a feed gas mixture of 89.5% CH_4 and 10.5% Ar was introduced with a gas hourly space velocity of 1500 mL g^{-1} h^{-1}. The effluent was analyzed on-line by gas chromatographs.

3. Results and discussion

3.1. Characterization of HZSM-5 zeolites

Figure 1 illustrates the XRD patterns of the parent HZSM-5, HZSM-5-H and HZSM-5-S. Clearly, the hydrothermal treatment in water led to remarkable loss of crystallinity of the parent zeolite. While, the HZSM-5-S showed pronouncedly intensive diffractions at $2\theta = 8°$ and 9°,indicating the occurrence of recrystallization during hydrothermal post-synthesis in NaOH aqueous solution.

Figure 2 shows the N_2 adsorption-desorption isotherms of the HZSM-5 samples, and the framework compositions and textural properties are summarized in table 1. N_2 adsorption of the parent HZSM-5 represented type I isotherm with a limited uptake of N_2 at higher relative pressures, typical for microporous materials without significant mesoporosity. Calculations by the t-plot method suggested that the majority of the surface area is contributed by the micropores. The increase in mesopore volume coupled with the pronounced hysteresis loop in the isotherm of HZSM-5-H clearly indicated that mesopores were developed during the hydrothermal treatment. Meanwhile, the considerable increase in the relative resonance intensity of surface silanol measured by ^{29}Si NMR further suggested the occurrence of severe extraction of tetrahedral Al from the zeolite lattices, resulting in the formation of more hydroxyl nests. The significant decreases in the surface area and pore volume of the micropores could be apparently attributed to the blockage of the micropores with debris from the partial amorphization and the aluminum extraction of the framework. Whereas, post-synthesis treatment of the parent HZSM-5 in NaOH aqueous solution also resulted in mild dealumination, but only a marginal increase in the intensity of Si-OH was observed. No hysteresis loop, representing the creation of mesopores, appeared in the isotherm of HZSM-5-S. This indicates that the vacancies in the framework (left by the expelled framework aluminum) were healed by the reincorporation of the Si and Al species dissolved in the NaOH solution during the post-synthesis treatment. This dynamic extraction and reincorporation effect stabilizes the HZSM-5 framework, prevents mesopores formation and finally leads to more homogeneous pore surface. Moreover, both the micropores surface area and the micropores volume increased, suggesting that the original microporous structure could be improved by the removal of non-framework materials within the zeolite channels during the post-synthesis treatment.

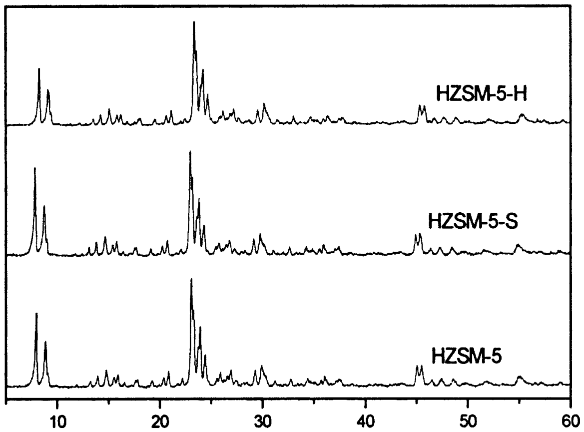

Figure 1. XRD patterns of the HZSM-5 samples.

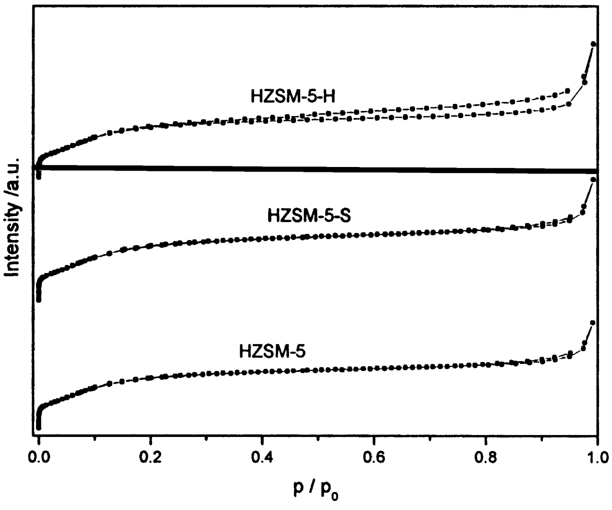

Figure 2. N_2 adsorption-desorption isotherms of the HZSM-5 samples.

The role of NaOH solution as a “channel sweeper” during the post-synthesis treatment are further confirmed by the ^{27}Al NMR spectra as shown in figure 3. For the parent HZSM-5, the resonance signal at 0 ppm assigned to octahedral Al species was clearly discerned, indicative of the presence of non-framework aluminum. After hydrothermal treatment in water, the resonance

Table 1
Framework composition and textural properties of HZSM-5 samples

Sample	Si/Al[a]	I_{silanol}[a] (% area)	S_{BET}[b] ($m^2 g^{-1}$)	S_{micro}[c] ($m^2 g^{-1}$)	V_{micro}[c] ($cm^3 g^{-1}$)	V_{meso}[d] ($cm^3 g^{-1}$)
HZSM-5	28.6	1.90	364	305	0.14	0.16
HZSM-5-H	39.7	2.36	375	272	0.13	0.20
HZSM-5-S	35.8	1.92	387	321	0.15	0.17

[a] Measured by ^{29}Si MAS NMR.
[b] BET method.
[c] t-plot method.
[d] BJH method.

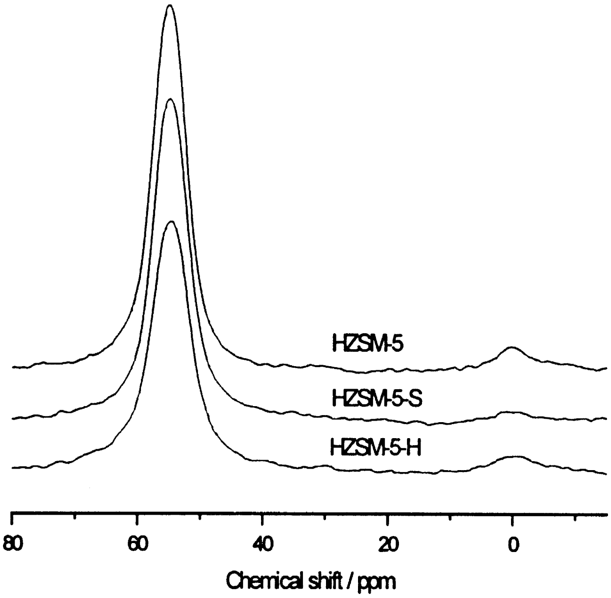

Figure 3. ^{27}Al MAS NMR spectra of the HZSM-5 samples.

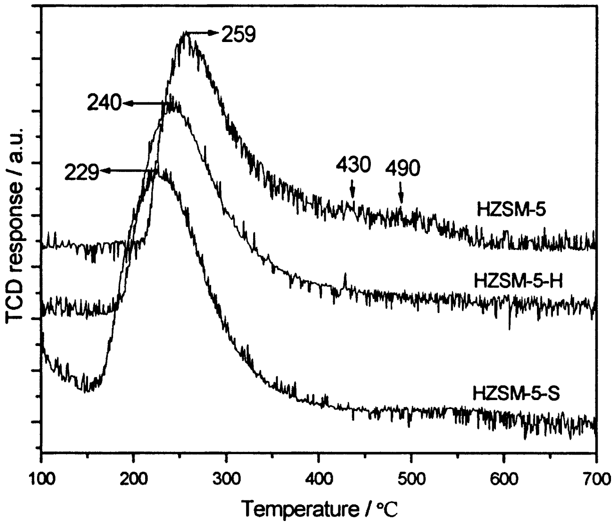

Figure 4. NH_3-TPD profiles of the HZSM-5 samples.

signal at 0 ppm become broader, and the peak at 55 ppm, attributed to tetrahedral Al species, dramatically decreased in intensity due to severe removal of framework aluminum. In contrast, the lowest non-framework Al and only slight decrease in the intensity of the tetrahedral Al species have been observed for the HZSM-5-S, implying that the original and as-made non-framework aluminum could be removed by reacting with NaOH solution during the hydrothermal post-synthesis.

Figure 4 illustrates the NH_3-TPD profiles of the HZSM-5 samples. The NH_3-TPD profile of the parent HZSM-5 shows a dominant NH_3 desorption peak at 259 °C with two weak shoulders at 430–490 °C, indicating the presence of acidic complexes with various acidic strength. Both hydrothermal treatment in water and hydrothermal post-synthesis in NaOH solution caused the major desorption peaks of ammonia shift to lower temperatures. Hydrothermal treatment with steam caused extraction of Al atoms, associated with the strong Brönsted-acid sites from their crystallographic positions, leading to the formation of acid centers with moderate acidic strength. In principle, the post-synthesis treatment in aqueous NaOH solution is more effective to reduce the acidic sites, but the good accessibility of micropores and the efficient reincorporation of Al species into the framework resulted in well-distributed acidic sites.

3.2. Methane dehydroaromatization

The catalytic behavior of the Mo/HZSM-5 catalysts for methane dehydroaromatization reactions is shown in figure 5. Obviously, the Mo/HZSM-5-S catalyst exhibited much higher CH_4 conversion and less coke deposition, resulting in significant improvement in the selectivity toward aromatics and catalytic durability. In contrast, heavy coke deposition was observed on the Mo/HZSM-5-H catalyst, leading to pronounced decrease in the methane conversion and selectivity to aromatics with time on stream. The hydrothermal treatment of the commercial zeolite caused heavy structural distortion, partial blockage of microspores and creation of substantial mesopores, thus reducing the shape-selectivity effect of ZSM-5 zeolites. Hydrothermal post-synthesis treatment of the parent HZSM-5 with the

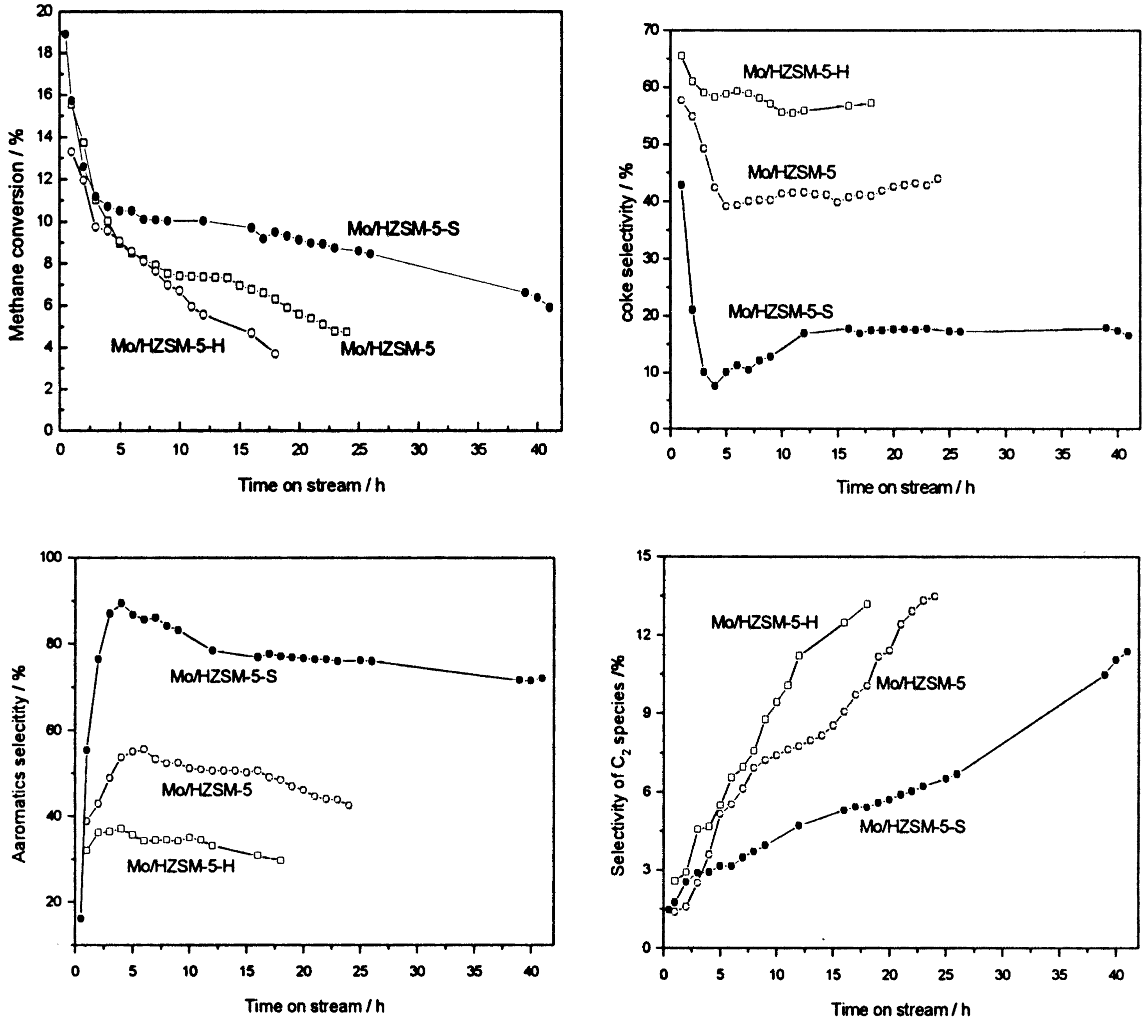

Figure 5. Methane conversion and products selectivities with time on stream. Experimental conditions: 700 °C; 0.2 g Mo/ZSM-5 catalysts; 89.5% CH_4 + 10.5% Ar; GHSV: 1500 mL g^{-1} h^{-1}.

NaOH aqueous solution not only effectively eliminated the strong acid sites (responsible for coke formation) without the risk of structure degradation, but also increased the accessibility of micropores by the removal of non-framework materials within ZSM-5 pore channels. Consequently, much higher benzene yield and rather prolonged catalytic stability were achieved over the Mo/HZSM-5-S catalyst for MDA reaction.

4. Conclusion

Restructuring of commercial HZSM-5 zeolites by hydrothermal post-synthesis treatment in NaOH solution greatly modified the microporous structure and the acidity. The occurrence of recrystallization and the efficient incorporation and extraction of the framework Al not only stabilize the framework with high crystallinity, but also prevent the creation of substantial extrapores. The hydrothermal post-synthesis treatment only causes moderate dealumination of the parent HZSM-5 and effectively removes the original or as-made debris blocking the zeolite channels, leading to a good accessibility of micropores. Consequently, the restructured Mo/ZSM-5 catalyst showed significant improvement in both catalytic durability and selectivity to aromatics in the methane dehydroaromatization reaction.

References

[1] Y. Xu, X. Bao and L. Lin, J. Catal. 216 (2003) 386.

[2] Y. Shu, H. Ma, R. Ohnishi and M. Ichikawa, Chem. Commun. (2003) 86.

[3] Y. Lu, D. Ma, Z. Xu, Z. Tian, X. Bao and L. Lin, Chem. Commun. (2001) 2048.

[4] Y. Xu and L. Lin, Appl. Catal. A 188 (1999) 53.

[5] D. Ma, Y. Lu, L. Su, Z. Xu, Z. Tian, Y. Xu, L. Lin and X. Bao, J. Phys. Chem. B 106 (2002) 8524.

[6] W. Ding, G.D. Meitzner and E. Iglesia, J. Catal. 206 (2002) 14.

[7] J.C. Groen, J.C. Jansen, J.A. Moulijn and J. Perez-Ramirez, J. Phys. Chem. B 108 (2004) 13062.

[8] L. Su, L. Liu, J. Zhuang, H. Wang, Y. Li, W. Shen, Y. Xu and X. Bao, Catal. Lett. 91 (2003) 156.