

Enhancing the Deactivation Durability of Nano-sized HZSM-5 for Aromatization by Adjusting its Ratio of Lewis/Bronsted Acid Sites

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Abstract: Ratio of Lewis/Bronsted acid sites (Cl/Cb) on the surface of nano-sized HZSM-5 was successfully manipulated by means of steaming and acid leaching. Significant enhancement of the deactivation durability of nano-sized HZSM-5 in the aromatization of fluid catalytic cracking (FCC) gasoline olefins seems to be closely related to the increase of Lewis/Bronsted acid sites ratio.

Keywords: Lewis acid, Bronsted acid, nano-sized HZSM-5, aromatization, gasoline.

Nano-sized zeolites have special physicochemical properties compared to micron-sized ones^{1,2}. Recently, we have demonstrated the effectiveness and the remarkable deactivation durability of nano-sized HZSM-5 in converting the olefins of FCC gasoline to high octane number alkylbenzenes³. The role of zeolitic acidity is an intensively studied topic in the aromatizations of light hydrocarbons over micron-sized HZSM-5. But it is seldom reported for the aromatization of gasoline olefins over nano-sized HZSM-5 so far. Therefore, this paper focused on the manipulation of the acidity of a nano-sized HZSM-5 by steaming and acid leaching, as well as the relationship between acidity and performance of the nano-sized HZSM-5 in converting the olefins of gasoline to aromatics.

Experimental

Five catalyst samples were prepared as follows: NaZSM-5 powder with crystal size of 20-50 nm and Si/Al atomic ratio of 25 was extruded with amorphous alumina into $\phi 1 \times (2 \sim 3)$ cylindrical pellet. After being dried at 110 °C and calcined in air at 540 °C for 3 h, the product was NH₄⁺-exchanged with 0.6 mol/L NH₄NO₃ solution under ambient condition, then dried and calcined to obtain HZSM-5. HZSM-5 was leached by a 0.4 mol/L HNO₃ solution for 24 h under ambient condition, then washed until pH approached to 7.0, and then dried and calcined to obtain Sample A. Sample B and C were prepared by steaming sample A with deionized water and 0.5 mol/L ammonia solution at 550 °C for 3 h

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in a fixed-bed reactor. Sample D and E were prepared by leaching sample B and C with 0.4 mol/L HNO₃ solution for 12 h (followed by drying and calcining), respectively.

The acidity of the catalyst samples was characterized by pyridine-IR spectroscopy. The catalytic performance of these samples was evaluated by the conversion of olefins of FCC gasoline to aromatics in a fixed-bed reactor operated at 370 °C, 3.0MPa, H₂/oil volumetric ratio at 600, WHSV_{oil} at 3 h⁻¹. The feed oil consists of 50% paraffins, 39% olefins, and 11% aromatics on volumetric basis. The product was analyzed with a GC (SRI8610) equipped with capillary column and FID.

Results and Discussion

Acidity manipulation of nano-sized HZSM-5

It can be seen in **Table 1**, steaming itself is a powerful method in eliminating both Brønsted (B) and Lewis (L) acid site on nano-sized HZSM-5 surface. After steaming at selected conditions, the parent nano-sized HZSM-5 loses approximately half of its total acid sites, but the ratio of Cl/Cb increases notably from 1.39 to 2.00 (sample B). Interestingly, sample B and C have quite different total acid sites but practically similar ratio of Cl/Cb. On the other hand, sample D and E have generally the same total acid sites but quite different ratio of Cl/Cb. It seems that the presence of NH₃ in steam has at least two effects: one is to hinder the removal of framework aluminum (related to B site), the other is to induce non-framework aluminum to form Lewis sites, which are removable upon acid leaching.

Table 1 The acidity of the samples

Sample	Preparation comments	Total acidity (Cb+Cl,mmol/g)	B acidity (Cb,mmol/g)	L acidity (Cl,mmol/g)	Cl/Cb
A	Parent	1.23	0.52	0.72	1.39
B	Steam A	0.65	0.22	0.44	2.00
C	Steam A with NH ₃	0.90	0.30	0.59	1.97
D	Acid-leach B	0.73	0.21	0.51	2.43
E	Acid-leach C	0.75	0.25	0.49	1.96

Catalytic performance of various nano-sized HZSM-5 catalysts

As shown in **Figure 1**, the parent catalyst possesses higher initial catalytic activity by less olefins and more aromatics in its initial product oil. However, the superiority of the parent catalyst faded away quickly and disappeared completely after 20 h on stream, this indicated that the catalyst be deactivated by coke deposition. On the contrary, those steamed catalysts all exhibit strong ability in resisting deactivation, due to the removal of the strongest acid sites on zeolite surface^{4,5}. In addition, the changing trend of olefin content and aromatic content against time means that aromatization is the main but not the only route for olefin conversion.

Effect of Cl/Cb ratio on converting gasoline olefins to aromatics

The synergetic effect between Brønsted acid sites and Lewis acid sites in catalyzing the aromatization of light hydrocarbons has been described in many literatures^{6,7}. The present work serves to illustrate how important the ratio of the two kinds of acid sites is. For this purpose, we define:

$$A = (A_{6h} - A_{54h}) / A_{6h}; \quad O = (O_{54h} - O_{6h}) / O_{6h}$$

Wherein, A_t and O_t stand for aromatic content (wt%) and olefin content (wt%) at t hours on stream, respectively. Thus higher ψ_A and ψ_O mean more aromatic loss and more olefin rebound.

ψ_A and ψ_O were plotted against Cl/Cb ratio in **Figure 2**. For the convenience of comparison, the as-treated catalysts are grouped and compared with A. In **Figure 2** (a), catalyst B and C are obtained by only steaming, therefore the non-framework aluminum species remain in their intracrystal channels. They have similar Cl/Cb ratio but quite different total acid amount ($C > B$). In **Figure 2** (b), catalyst D and E are obtained by steaming and acid leaching, therefore the non-framework aluminum species in their intracrystal channels are supposed to be removed to some extent. They have similar total acid amount but quite different Cl/Cb ratio ($D > E$).

Figure 1 Content of olefins and aromatics in FCC gasoline treated by various catalysts

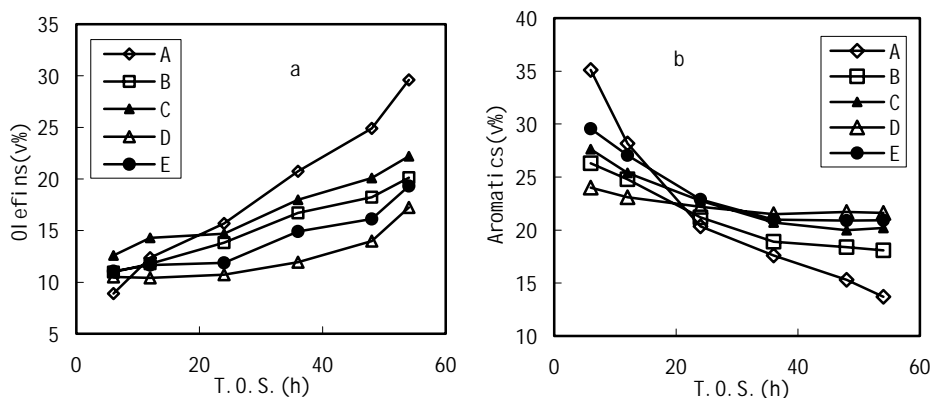
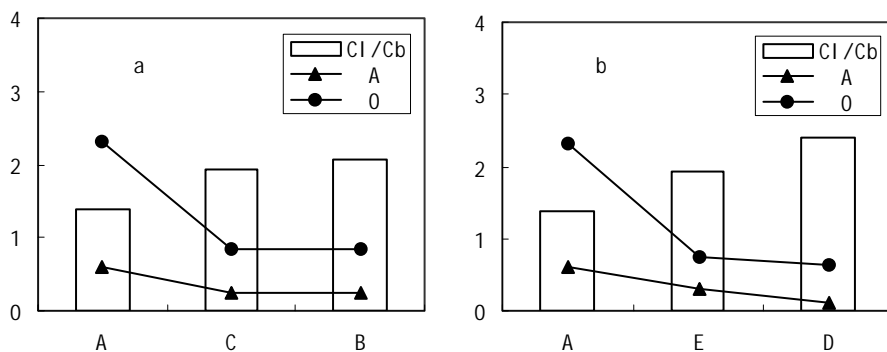


Figure 2 Aromatic loss (ψ_A) and olefin rebound (ψ_O) of the catalysts



Concisely, the higher the Cl/Cb ratio of the catalysts, the less the aromatic loss and the olefin rebound can be obtained. That is, the stability of nano-sized HZSM-5 catalytic activity increases with the ratio of Cl/Cb. Best stability can be found in catalyst D with Cl/Cb ratio of 2.43. This phenomenon implies that suitable ratio of Brønsted acid site and Lewis acid site is needed to keep each elementary reaction in the desired reaction chain (reactants to aromatics) proceeding at suitable speeds, so as to avoid the overstock of intermediates which may accelerate side-reaction chain of coke formation.

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