



Short communication

On-stream stability enhancement of HZSM-5 based fluid catalytic cracking naphtha hydro-upgrading catalyst via magnesium modification

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ABSTRACT

On-stream stability of fluid catalytic cracking (FCC) naphtha hydro-upgrading catalysts that convert olefins into high-octane isoparaffins and aromatics is crucial for guaranteeing the long-term operation of industrial units, and therefore suppressing catalyst deactivation due to coking becomes the focus of FCC naphtha hydro-upgrading process and catalyst development. Here we report a simple and novel strategy to enhance the on-stream stability of a HZSM-5 based FCC naphtha hydro-upgrading catalyst by magnesium modification. The characterization and catalytic test results showed that the incorporation of a suitable amount of MgO can adjust the ratio of Lewis acid sites to Brønsted ones and thereby significantly improve stability of the resulting catalyst.

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1. Introduction

Formation and retention of carbonaceous residua, generally referred as coke that is responsible for catalyst deactivation, either in pore channels or on outer surfaces of zeolite-based catalysts, are frequently encountered in many catalytic processes, such as hydrocarbon isomerization and aromatization. Therefore, inhibiting catalyst deactivation due to coking to extend catalyst life is one of the primary challenges in the development of many catalytic processes, and for this reason numerous efforts have been made [1–3]. It is well known that acid sites of zeolite-based catalysts are not only active centers for target reaction but also coke formation sites. The previous studies [4–6] showed that introduction of metal elements could influence both the acidity and texture characteristics of the resulting catalysts and therefore benefit the catalytic performance and lessen catalyst deactivation. Although many results had been reported, the effects of variation in acid types (i.e. Brønsted (B) and Lewis (L) acid sites) resulting from metal introduction on the catalytic performance of zeolite-based catalysts are scarcely touched. In the previous work [7–9], we proposed a HZSM-5 zeolite based catalyst system to convert olefins in fluid catalytic cracking (FCC) naphtha into isoparaffins and aromatics that have research octane number (RON) higher than or comparable to the corresponding olefins and successfully developed a FCC naphtha hydro-upgrading process referred as GARDES that has been widely used in

industry [10–12]. To improve the on-stream stability of the HZSM-5 zeolite based catalyst, we exploited a combined post-treatment method consisting of steaming and citric acid leaching. While having superior olefin reduction ability, excellent RON preservability and high liquid product yield, the HZSM-5 based catalyst system suffered from slow deactivation due to coking, which becomes a major restricting factor for the long term operation of the process. To overcome this shortage, herein we present a novel method to introduce magnesium into HZSM-5 for enhancing the on-stream stability of the HZSM-5 based isomerization and aromatization catalyst.

2. Experimental

The NiMo/HZSM-5- γ -Al₂O₃ catalyst referred as C-0 was prepared according to the method described elsewhere [13]. Catalyst C-0 was further impregnated with an aqueous solutions of magnesium nitrate, dried at 110 °C overnight, and calcinated at 480 °C for 4 h, and the thus obtained MgNiMo/HZSM-5- γ -Al₂O₃ catalysts with MgO loadings at 0.5, 1.0, and 3.0 wt.% were denoted as C-0.5, C-1.0 and C-3.0, respectively. The characterization and catalytic test methods were described elsewhere [11]. The properties of the feeding FCC naphtha are shown in Table 1. The aromatization activity and selectivity, and hydroisomerization activity are defined as follows: aromatization activity is expressed in terms of the increment in the i-paraffin content in the product, aromatization selectivity is represented by the ratio of the increment in the aromatics content in the product to the decrement in the olefin content in the product, and hydroisomerization activity is defined in terms of the increment in the i-paraffin content in the product.

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Table 1
Properties of the feeding FCC naphtha.

Density (g/cm ³)	S (μg/g)	Benzene (v%)	RON	Lumped composition (v%)				
				n-Paraffins	i-Paraffins	Olefins	Naphthenes	Aromatics
0.715	105	0.64	93.2	6.45	21.73	39.92	8.65	23.25

3. Results and discussion

3.1. Effects of Mg incorporation on catalytic performance

The effects of Mg incorporation on the hydro-upgrading performance of the catalysts are shown in Fig. 1. While all of the catalysts showed outstanding olefin reduction, hydroisomerization and aromatization activities, they differed from each other in their initial activities and deactivation rates. Catalyst C-0 without MgO incorporation features the highest aromatization activity and moderate hydroisomerization activity, but the rapidest deactivation rate; catalysts C-1.0 and C-3.0 loaded with 1.0 and 3.0 wt.% MgO showed excellent stability but relatively poorer olefin reduction and aromatization activities; and catalyst C-0.5 loaded with 0.5 wt.% MgO exhibited the highest aromatization selectivity, moderate hydroisomerization activity and the best on-stream stability.

3.2. Effects of Mg incorporation on catalyst physicochemical properties

3.2.1. Textural properties

Zeolite pore structure plays an important role in shape-selective reactions, both target ones and unwanted coke deposition ones [14]. For this reason, the textural properties of the catalysts were measured and the results are shown in Table 2. As seen, the specific surface areas, total pore volumes and average pore diameters of the catalysts

decreased with the increasing MgO loading. Even though, the catalyst with a MgO loading of 3.0 wt.% had a BET specific surface area as high as 288.7 m²/g, signifying that the incorporation of MgO does not significantly affect the textural properties of the catalysts and thus indicating that the textural parameters do not account for the distinctly different catalytic and deactivation performance of the catalysts.

3.2.2. Quantity and strength of acid sites

The effects of Mg incorporation on the acid quantities and strength distributions of the catalysts were studied by temperature-programmed desorption of ammonia (NH₃-TPD) and the results are shown in Fig. 2. For each curve in the figure, two peaks can be distinguished: the one at higher temperature ascribed to strong acid sites and the other at lower temperature to weak acid sites. The area of each peak is proportional to the number of the corresponding acid sites. With the increasing MgO loading, strong acid sites gradually decrease (inset in Fig. 2), weak ones gradually increase, and the location of the peak representing weak acid sites shifts to the lower temperature side; particularly, when the MgO loading was at 3.0 wt.%, the strong acid sites decrease dramatically and the weak ones reached the maximum. For Mg-ZSM-5 zeolites prepared via the solid-state reaction of HZSM-5 with magnesium chloride, Li et al. [15] observed the similar phenomenon. They suggested that this is because Mg²⁺ reacted with the strong acidic OH groups in HZSM-5 to form Mg(OH)⁺ that has only weak acidity. According to de Lucas et al. [16] and Song et al. [17], olefin aromatization activity increases with the increasing number of strong acid sites, so the NiMo/HZSM-5 catalyst with a MgO loading of 3.0 wt.% has the lowest aromatization activity because of its least strong acid sites, as shown in Figs. 1 and 2. Therefore, the changes in the acid quantity and strength distribution of the catalysts due to MgO incorporation are the factor influencing the catalytic performance.

3.2.3. Type of acid sites

It is also known that the type of acid sites also impacts the catalyst performance. For FCC naphtha hydro-upgrading, both hydroisomerization and aromatization are pursued reactions for olefin reduction and octane preservation, but they proceed in quite different paths: (1) according to the mechanism shown in Scheme 1(a) [18], isomerization of *n*-alkanes over metal-acid catalysts proceeds through five steps, among which steps (i) and (v) occur over metal sites, whereas steps (ii), (iii) and (iv) occur on the acid sites of the catalyst; (2) according to the classical aromatization mechanism shown in Scheme 1(b) [19], carbonium ions are firstly formed over L acid sites (step i) and then transformed to olefins on B acid sites (step ii); after the successive oligomerization (step iii) and cyclization (step iv) on B acid sites, aromatics are finally formed via the dehydrogenation of naphthene on L acid sites (step v). Therefore, the synergism of L and B acid sites is

Table 2
Textural characteristics of the catalysts with different MgO loadings.

Catalyst	Surface area (m ² /g)			Pore volume (cm ³ /g)		Average pore diameter (nm)
	BET	Micropores	Mesopores	Total	Micropores	
C-0	313.4	215.3	98.1	0.250	0.180	4.38
C-0.5	300.8	213.7	87.1	0.243	0.176	4.37
C-1.0	299.0	211.8	87.2	0.242	0.175	4.29
C-3.0	288.7	209.1	79.6	0.231	0.163	4.29

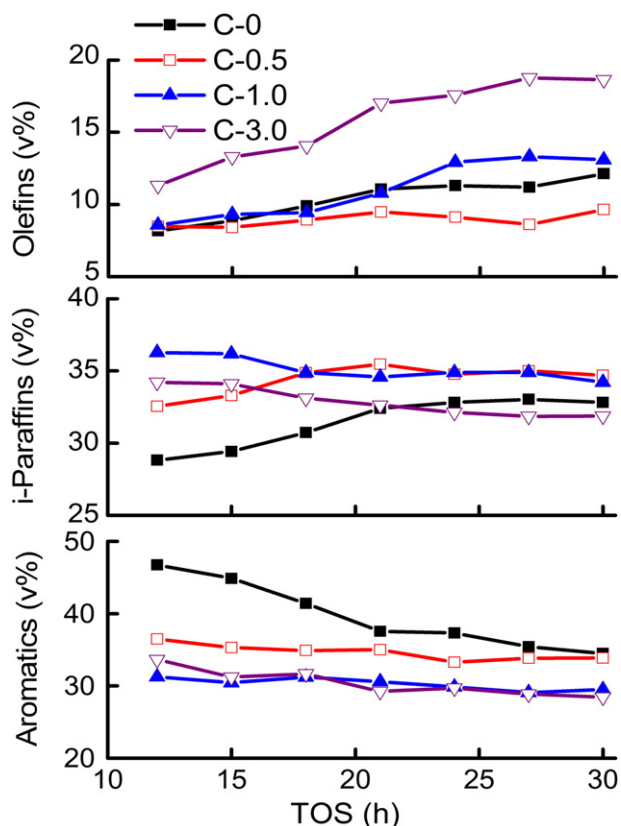


Fig. 1. FCC naphtha hydro-upgrading results of the catalysts with different MgO loadings.

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