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ORIGINAL RESEARCH ARTICLE

Liquid deposition modification of nano-ZSM-5 zeolite and catalytic performance in aromatization of Hexene-1

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ABSTRACT

The Olefin aromatization is an important method for the upgrade of catalytic cracking (FCC) gasoline and production of fuel oil with high octane number. The nano-ZSM-5 zeolite was synthesized via a seed-induced method, a series of modified nano-ZSM-5 zeolite samples with different Ga deposition amount were prepared by Ga liquid deposition method. The XRD, N_2 physical adsorption, SEM, TEM, XPS, H_2-TPR and Py-IR measurements were used to characterize the morphology, textural properties and acidity of the modified ZSM-5 zeolites. The catalytic performance of the Hexene-1 aromatization was evaluated on a fixed-bed microreactor. The effects of Ga modification on the physicochemical and catalytic performance of nano-ZSM-5 zeolites were investigated. The Ga species in the modified nano-ZSM-5 zeolites mainly exist as the form of Ga_2O_3 and GaO^+, which provide strong Lewis acid sites. The aromatics selectivity over Ga modified nano-ZSM-5 zeolite in the Hexene-1 aromatization was significantly increased, which could be attributed to the improvement of the dehydrogenation activity. The selectivity for aromatics over the Ga4.2/NZ5 catalyst with suitable Ga deposition amount reached 55.4%.

Keywords: Nanosized ZSM-5 Zeolite; Ga Modification; Liquid Deposition; Hexene-1; Aromatization

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1. Introduction

With the rapid development of China's automobile industry, the demand for fuel oil such as gasoline is increasing day by day. At present, catalytic cracking (FCC) gasoline is still the main vehicle fuel oil used all over the world, especially in China, the proportion of FCC gasoline is as high as about 80%. Due to the high olefin content in FCC gasoline, insufficient combustion will lead to a series of environmental pollution problems such as high PM2.5 content in automobile exhaust and photochemical smoke[1]. Therefore, reducing the olefin content in FCC gasoline to improve fuel quality has become an urgent problem to be solved. Aromatics are not only gasoline blending components with high octane number, but also important basic chemical raw materials. Therefore, converting olefins in FCC gasoline into high value-added aromatics through aromatization reaction can not only reduce the olefin content in gasoline and maintain or improve the octane number of gasoline, but also provide an effective channel for the production of aromatics. The research and development of high-efficiency catalyst is the technical core of this process.

ZSM-5 zeolite is widely used in petrochemical and other fields as an efficient catalyst because of its unique three-dimensional cross pore structure, rich active centers and good hydrothermal stability[2,3]. However, ZSM-5 zeolite with micron scale and single micro-porous structure will limit the formation and diffusion of transition intermediates and products in the pores in the acid catalytic reaction, resulting in the rapid deactivation of the zeolite due to coking and carbon deposition. The strong Brønsted acid center of aluminosilicate zeolite is easy to lead to side reactions such as cracking of long-chain olefin intermediates generated in the process of olefin aromatization, so as to reduce the selectivity of aromatics. The pore characteristics and acidity of ZSM-5 zeolite can be adjusted by reducing the particle size of zeolite and adopting the modification method of secondary synthesis[4–6]. The existing template method for synthesizing nano ZSM-5 still has many environmental problems such as large amount of organic template, high cost and large amount of nitrogen-containing wastewater. Therefore, it is necessary to establish a new green and efficient method for the synthesis of nano ZSM-5 zeolite. Methods for adjusting the acidity of zeolite include ion exchange method, isomorphic replacement method and liquid deposition method[7–11]. Although acid dealumination modification will remove some skeleton aluminum atoms of zeolite and reduce strong acid sites, it will destroy the skeleton stability of zeolite and produce a large amount of acid wastewater. The introduction of metal species by ion exchange method is limited, and the acid regulation of the catalyst and the improvement of catalytic reaction performance are small. The isomorphic substitution modification reduces the acid strength of zeolite by introducing heteroatoms into the zeolite skeleton, and forms skeleton defect sites to a certain extent.

Introducing Ga species into zeolite by liquid phase deposition is the simplest and effective modification method to adjust its acid strength, Brosted and Lewis acid site density and the ratio of two active sites[12]. In the process of liquid phase deposition, Ga species will cover some strong acid sites of zeolite, and form active Ga species providing strong L acid, promote the dehydrogenation rate control step in the aromatization reaction process, and effectively improve its catalytic aromatization performance.

In this paper, nano ZSM-5 zeolite synthesized by prefabricated seed method was modified by Ga liquid deposition, and the effects of Ga modification on the pore characteristics, acidity and catalytic aromatization of Hexene-1 of nano ZSM-5 zeolite were studied.

2. Experiment

2.1 Synthesis of nano ZSM-5 zeolite

The mixture of four propyl ammonium hydroxide, aluminum isopropyl alcohol, tetraethyl orthosilicate and deionized water were mixed according to the ratio of 35.7 TPAOH:100 SiO_2:Al_2O_3:1,083 H_2O (mole ratio). After mixing at room temperature, the mixed gel was prepared and then transferred into the crystallization reactor to heat the 30 min by microwave radiation. Obtain the preformed crystal seed for use. A uniform gel was prepared by mixing sodium aluminate, silica sol, sodium hydroxide and two deionized water, adding the preformed seed and then crystallizing 6 h at 180 °C. The crystallization product is centrifuged, dried, roasted, ion exchanged with NH_4NO_3 solution, dried and roasted to obtain H-type ZSM-5 zeolite, which is recorded as NZ5.

2.2 Preparation of Ga modified nano ZSM-5 zeolite

A certain amount of H-type nano ZSM-5 zeolite sample (NZ5) prepared according to the method described in 2.1 is added to a certain concentration of $Ga(NO_3)_3$ solution, stirred at room temperature for 2 h, dried overnight, and calcined at 550 degrees Celsius for 3 h. The prepared Ga modified nano ZSM-5 zeolite is recorded as Ga*x*/NZ5, *x* is the mass percentage of Ga in the modified zeolite.

2.3 Evaluation of catalytic reaction performance

A fixed bed micro reactor was used to evaluate the catalytic performance of zeolite before and after modification for the aromatization of Hexene-1.

Weigh 1.0 g of 20–40 mesh catalyst, place it in the constant temperature zone of the reactor, and fill both ends with quartz sand. The reaction temperature was 480 degrees Celsius, the pressure was 0.5 MPa, the mass space velocity was 2.0 h^{-1}, and the flow rate of carrier gas (nitrogen) was 75 mL·min^{-1}. The reaction product was cooled in a low-temperature constant temperature bath, and the time when the first drop of liquid phase product appeared was recorded as zero time, and then the product was collected every 2 h. The composition of the reaction product was analyzed by GC-7900 installed with FID detector and PONA capillary column (50.0 m × 200 μm × 0.5 μm).

3. Experimental results and discussion

3.1Structural characterization and analysis of Ga modified nano ZSM-5 zeolite

Nano ZSM-5 zeolite (sample NZ5) and Ga4.2-NZ5 (Ga content of 4.2 wt.%) modified by Ga liquid deposition were characterized by SEM and TEM, as shown in **Figure 1**. Gallium oxide nano-clusters with a uniform size of about 2 nm can be observed on the surface of the modified sample Ga4.2-NZ5.

The nano ZSM-5 zeolite before and after liquid deposition modification with different Ga content were characterized by XRD. The XRD spectrum and relative crystallinity are shown in **Table 1** and **Figure 2**.

(a) (b) (c)

Figure 1. SEM and TEN images of nanosized ZSM-5 zeolit **(a, b)** and TEM image of Ga4.2-NZ5 sample modified by Ga-impregnation **(c)**.

Table 1. Relative crystallinity, textural properties and chemical composition of ZSM-5 zeolite samples modified by Ga-impregnation

Sample	**Relative crystallinity^a /%**	**Chemical composition**			**Ga /(wt%)**	**Surface area /(m^2·g^{-1})**	
		Si/Al^b	**Si/Ga^c**	**Si(Me)^d**		**BET^f**	**Micropore^g**
HNZ5	100	48	—	48	0	386	74
Ga1.5/NZ5	96	48	77	30	2.5	358	70
Ga2.1/NZ5	96	48	58	26	3.3	352	69
Ga4.2/NZ5	96	48	27	17	5.1	336	55

Note: ^{a}Relative crystallinity (RC) calculated from XRD patterns; ^{b}obtained by XRF method; ^{c}determined from ICP; ^{d}Me corresponds to the Al and Ga; ^{e}mass percent content of Ga on the surface determined from XPS; ^{f}BET method; gt-plot method.

It can be seen from **Figure 2** that the XRD spectrum of the modified zeolite still has only the characteristic diffraction peak of MFI topology, and there is no spectral peak of Ga_2O_3, indicating that Ga species are highly dispersed in ZSM-5 zeolite. It can be seen from **Table 1** that the relative crystallinity of ZSM-5 zeolite modified by Ga decreases slightly, and its specific surface area decreases with the increase of Ga deposition, because gallium species block some pores of the zeolite. In addition, the Ga content on the outer surface of Ga modified zeolite was analyzed by X-ray photoelectron spectroscopy (XPS), and compared with the Ga content of zeolite measured by ICP method, it was found that the Ga content on the outer surface of zeolite was higher, indicating that Ga species were mainly distributed on the outer surface of zeolite.

Ga modification can not only form Ga_2O_3 nano clusters on the surface of zeolite, but also form Gao^+ species with dehydrogenation activity[13]. In order to prove the existence of Gao$^+$ active species in the zeolite modified by Ga liquid phase deposition, the samples were characterized by H_2-TPR and XPS. The results are shown in **Figure 3**, **Figure 4** and **Table 2** respectively.

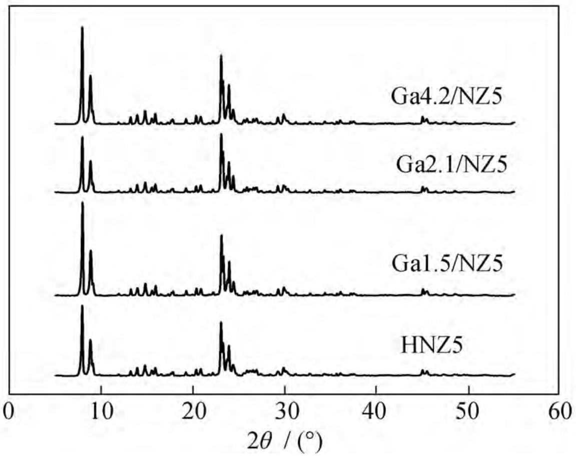


Figure 2. XRD patterns of nanosized ZSM-5 zeolite samples modified by Ga-impregnation.

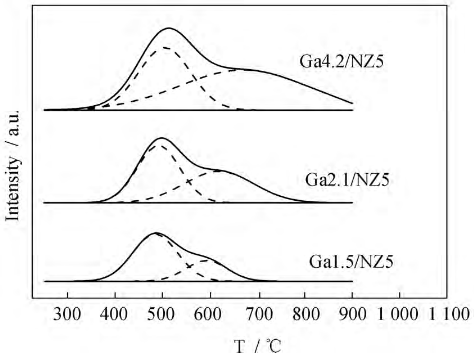


Figure 3. H_2-TPR profiles of nanosized ZSM-5 zeolite samples modified by Ga-impregnation.

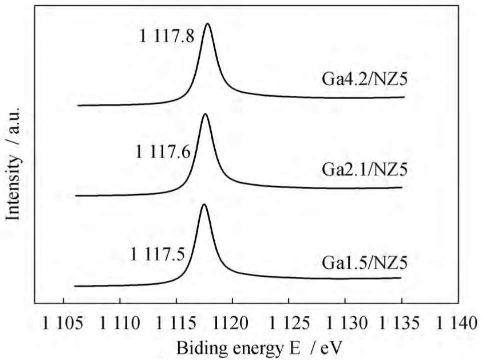


Figure 4. Ga $2p^{3/2}$ XPS spectra of nanosized ZSM-5 zeolite samples modified by Ga-impregnation.

It can be seen from **Figure 3** and **Table 2** that in the H_2-TPR curve of modified Ga*x*/NZ5 series samples, there are reduction peaks corresponding to Ga_2O_3 and active Gao$^+$ species with strong interaction with the negative charge of zeolite skeleton at 350–600 °C and 500–800 °C respectively. With the increase of Ga deposition, the amount of hydrogen consumed when Ga_2O_3 and Gao$^+$ species are restored increases. The reduction temperature of Ga_2O_3 increases slightly with the increase of Ga deposition amount, from 486 °C to 501 °C, which may be due to the increase of the size of Ga_2O_3 nano clusters formed when the deposition amount of Ga increases, and thus it may be more difficult to be restored. When the deposition amount of Ga increases from 1.5% to 4.2%, the reduction temperature of corresponding Gao$^+$ species in Ga*x*/NZ5 series modified samples increases significantly from 602 °C to 693 °C, which is due to the enhanced interaction between Gao$^+$ species and the negative charge of zeolite skeleton[14].

Table 2. H_2-TPR data of nanosized ZSM-5 zeolite samples modified by Ga-impregnation

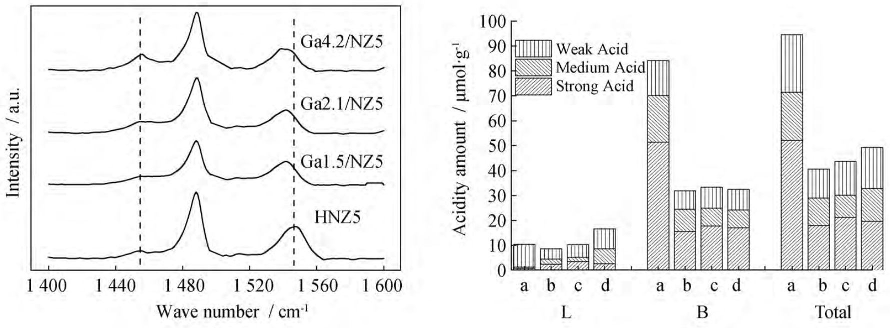
Sample	**Temperature/℃**		**Consumption of H_2/($\times 10^{-5}$ mol·g^{-1})**		
	L.T.	H.T.	$Ga_2O_3 \to Ga_2O$	$GaO^+ \to Ga^+$	Total
Ga1.5/NZ5	486	602	8.71	3.29	12.00
Ga2.1/NZ5	489	636	12.11	7.89	20.00
Ga4.2/NZ5	501	693	15.82	15.52	31.34

It can be seen from **Figure 4** that with the increase of Ga deposition in the sample, the electron binding energy of Ga*x*/NZ5 series modified samples increases from 1117.5 eV to 1117.8 eV, which can be attributed to the strong interaction between more Gao$^+$ species and the negative charge of zeolite skeleton. It is consistent with the characterization results of H_2-TPR.

3.2 Characterization and analysis of acidity of Ga modified nano ZSM-5 zeolite

In order to study the effect of Ga liquid deposition modification on the acidity of nano ZSM-5 zeolite, the samples before and after modification were characterized by pyridine adsorption infrared spectroscopy (Py-IR). The results are shown in Figure 5.

It can be seen from **Figure 5(a)** that the Py-IR spectrum of the modified series of samples Ga*x*/NZ5 corresponds to the absorption peaks of acid sites of Brθsted near 1,545 cm^{-1} move towards low wave number, indicating that the acid intensity decreases. As can be seen from **Figure 5(b)**, the acid content of Brθsted of Ga modified zeolite decreased significantly. Due to partial Brθsted acid site is covered by the deposited Ga species, or the acid site of Brθsted in the pore cannot be detected due to blocking part of the pore of zeolite. The acid content of Brθsted of Ga modified Ga*x*/NZ5 series modified samples did not change significantly. However, with the increase of Ga deposition, the Lewis acid content and total acid content of the modified samples increased due to the formation of more Ga_2O_3 and active Gao$^+$ species.



(a) (b)

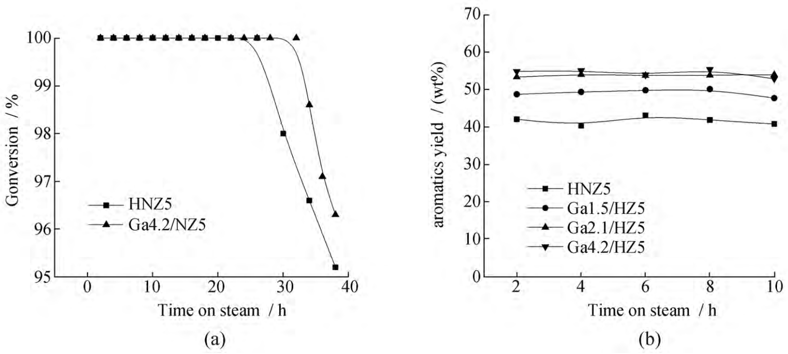
Figure 5. Py-IR spectra **(a)** and acid amount **(b)** of the nano-sized ZSM-5 zeolite samples modified by a. HNZ5, b. Ga1.5/NZ5, c. Ga2.1/NZ5, d. Ga4.2/NZ5.

3.3 Catalytic performance of Ga modified nano ZSM-5 zeolite for aromatization of Hexene-1

In order to explore the corresponding relationship between the structure and acidity of Ga modified nano ZSM-5 zeolite and its catalytic aromatization reaction performance, the catalytic performance of Ga liquid-phase deposition modified nano ZSM-5 was studied with Hexene-1 as a model compound. The results are shown in **Figure 6**.

It can be seen from **Figure 6(a)** that the modified zeolite Ga4.2/NZ5 catalyst has better catalytic stability than the unmodified ZSM-5 zeolite (HNZ5), and the conversion of Hexene-1 is still close to 100% at 35 h, which is due to the reduction of strong acid content and milder acidity of Ga modified molecular sieve, the deactivation of molecular sieve due to carbon deposition is inhibited.

It can be seen from **Figure 6(b)** that when Gax/



(a) (b)

Figure 6. Catalytic performance in Hexene-1 aromatization over the nanosized ZSM-5 zeolite samples modified by Ga-impregnated.

NZ5 series modified zeolite are used as catalysts, the total aromatics selectivity of Hexene-1 aromatization reaction is improved to varying degrees. When the deposition amount of Ga on ZSM-5 zeolite is 1.5% and 2.1% respectively, the corresponding catalysts Ga1.5/NZ5 and Ga2.1/NZ5 can greatly improve the selectivity of aromatics in the reaction products. When the deposition amount of Ga increases to 4.2%, the selectivity of Ga4.2/NZ5 catalyst for aromatics reached the maximum, up to 55.4%, which is that the active GaO^+ species with more strong L acid sites in Ga4.2/NZ5 catalyst promoted the dehydrogenation reaction.

4. Conclusion

The preformed seed method can not only greatly reduce the amount of organic template, but also synthesize nano ZSM-5 zeolite with regular morphology and high crystallinity. Liquid deposition modification is a simple and easy method to adjust the acidity of molecules. Because the liquid deposition modified GaZSM-5 not only weakens the strength of the acid site of Brθsted and inhibits the cracking reaction, but also forms an active GaO^+ species with strong Lewis acid site, improves the dehydrogenation activity of the zeolite catalyst, and therefore significantly improves the aromatics selectivity of the aromatization reaction of Hexene-1. This research work provides a useful idea for the improvement of acidity regulation and catalytic performance of zeolites.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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