

ROLE OF ZINC IN Zn-LOADED ZSM-5 ZEOLITES IN THE AROMATIZATION OF n-HEXANE

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Aromatization of n-hexane over zinc-modified ZSM-5 zeolites was investigated. It was shown that incorporation of zinc by ion exchange into cationic positions of NH₄-ZSM-5 zeolite causes acid-site strength redistribution and generation of new relatively strong Lewis acid sites in zeolite increasing the selectivity of n-hexane aromatization in comparison with the parent NH₄-ZSM-5 zeolite. Simultaneous presence of Lewis and Broensted acid sites in ZSM-5 zeolite does not affect the strength of Broensted acid sites in zeolite. For the activity/selectivity of aromatization of n-hexane on Zn-modified ZSM-5 zeolites, the amount of Zn and its localization in the cationic positions are decisive. The reaction of n-hexane can be also initiated by the Zn species alone in the cationic positions. ZnO species alone as an extra-framework phase was found inactive in the catalyst for aromatization of n-hexane. The influence of ZnO addition on the performance of pure ammonium forms of ZSM-5 zeolites in n-hexane conversion is a result of partial migration of zinc into cationic positions of zeolite by solid-state ion exchange.

Key words: ZnZSM-5; Acidity; Aromatization; n-Hexane; Solid-state ion exchange; Zeolites; Heterogeneous catalysis.

The transformation of lower hydrocarbons into aromatics over zeolites is an industrial important reaction. There has been continued interest in the design of catalysts for the effective utilization of C₁-C₄ alkanes as chemical feedstocks¹.

There are many authors who reported that introduction of zinc or gallium species into a zeolite significantly enhances the aromatization activity/selectivity of H-ZSM-5 (refs¹⁻¹³). In recent years there has been considerable interest in the mechanism of alkane activation with zeolite catalysts¹, but the activation step of lower alkanes aromatization is still a point of wide discussion. Mole and Anderson on the basis of the propane aromatization supposed that zinc located in the cationic positions catalyzes

the hydrid abstraction from alkane¹⁴. Other authors suggested that zinc or gallium species in the cationic positions catalyzes dehydrogenation of ethane^{4,13}, propane^{2,3,5,7-9,13}, butane^{3,13,15}, pentane^{13,16}, n-hexane¹³ and heptane¹². On the other hand, many authors^{16,17} supposed that zinc or gallium cations have no direct role in alkane activation.

It was also reported that mechanical mixtures of metal oxides (ZnO or Ga₂O₃) and H-ZSM-5 are highly active and selective in the aromatization of lower alkanes¹⁸⁻²⁰. Bhattachayra and Sivasanker¹⁸ reported that the aromatization of n-hexane over H-ZSM-5 is enhanced by the promoters ZnO and Ga₂O₃, while Fe₂O₃ and Cr₂O₃ decrease the aromatization. The role and the state of metallic species in mechanical mixtures under the reaction conditions have been also the subject of wide discussion¹⁹⁻²⁵. Kanai and Kawata¹⁹ concluded that the mechanical mixture of ZnO and NH₄-ZSM-5 is a bifunctional catalyst and that ZnO catalyzes dehydrogenation of n-hexane into hexene and of the oligomerized products into aromatics in the aromatization of n-hexane.

The influence of the preparation method on the location of zinc or gallium species inside or outside the channels and its role in the catalytic activity has not been sufficiently explained or has been controversially discussed so far^{4,9-11,15,26-28}.

To contribute to the mentioned discussion, we prepared catalysts using different zinc loading techniques (ion exchange, impregnation and mechanical admixing of ZnO) from Na and NH₄ forms of ZSM-5 zeolites and alumina in order to study relations between the state and position of Zn and the catalytic activity in the conversion of n-hexane.

EXPERIMENTAL

ZnZSM-5 catalysts with different amounts of zinc were prepared by ion exchange of NH₄-ZSM-5 (Si/Al = 14, 1.01 mmol Al/g) with aqueous solution of zinc acetate using 0.10, 0.28, 0.47, 1.46 and 4.68 mmol Zn²⁺/g catalyst in suspension for 4 h at 85 °C. NaZnZSM-5 catalyst was prepared in the same way from parent NaZSM-5 zeolite. Then the catalysts were thoroughly washed with distilled water and dried. The extent of the ion exchange was calculated from chemical analysis of Zn solutions before and after the ion exchange.

Mechanical mixtures containing the same amount of Zn as the 0.7 ZnZSM-5 catalyst were prepared by mechanical mixing of ZnO with NH₄-ZSM-5 (ZnO-NH₄-ZSM-5) and NaZSM-5 (ZnO-NaZSM-5). The ZnO-alumina catalyst was prepared by impregnation of alumina with a zinc acetate solution.

The acidity of the catalysts was determined by temperature programed desorption of ammonia (TPDA). Adsorption of ammonia was carried out at 220 °C after activation of samples for 1 h at 500 °C in a stream of helium. The quantity of desorbed ammonia (desorbing from 220 to 550 °C) was detected by titration of the excess of 0.1 M H₂SO₄. Broensted and Lewis

acid sites in the $\text{NH}_4\text{-ZSM-5}$ and 0.7 ZnZSM-5 samples were determined by FTIR using d_3 -acetonitrile as a probe molecule (details in ref.²⁹) sorbed at room temperature for 20 min at 1 333 Pa.

Conversion of n-hexane and disproportionation of toluene was performed in vapour phase, in a continuous glass flow microreactor with 100 mg of catalyst on-line connected with gas chromatograph, at atmospheric pressure in a stream of nitrogen (20 ml/min) saturated with n-hexane or toluene at 0 °C. Before the catalytic tests, the catalysts were activated *in situ* in a stream of dry air (50 ml/min) for 1 h at 450 °C. Conversion of n-hexane was carried out at 350 and 420 °C. Toluene disproportionation was performed at 380 °C. The reaction products were analyzed by gas chromatography using an of HP-1 capillary column (15 m \times 0.530 mm) and FID detector.

RESULTS AND DISCUSSION

Characteristics of the ion-exchanged ZnZSM-5 catalysts are given in Table I. It can be seen that in the catalysts with increasing amounts of Zn in cationic positions, the total conversion of n-hexane increases with a simultaneous increase in selectivity to aromatics. In the catalyst with the highest amount of Zn (0.7 ZnZSM-5), the total conversion achieved the level of conversion on the pure $\text{NH}_4\text{-ZSM-5}$ but the selectivity to aromatics is al-

TABLE I
Characteristics of the ion-exchanged catalysts

Catalyst	Zn mmol/g	Acidity ^a mmol/g	n-Hexane conver- sion at 420 °C, wt. %	Selectivity, %	
				aromatics	cracking products
$\text{NH}_4\text{-ZSM-5}$	0	0.91	42.4	4.9	91.5
		1.35 ^b 0.044 ^c			
0.17 ZnZSM-5	0.09	0.91	30.3	15.2	83.2
0.4 ZnZSM-5	0.20	0.90	33.9	30.7	68.1
0.46 ZnZSM-5	0.23	0.87	36.3	36.0	61.7
0.54 ZnZSM-5	0.27	0.80	41.2	42.0	55.1
0.7 ZnZSM-5	0.35	0.85	47.6	50.2	48.3
		0.55 ^b 0.52 ^c			
NaZnZSM-5	0.20	0.37	18.4	43.0	58.1

^a By TPDA. ^b Broensted acidity, by FTIR of adsorbed d_3 -acetonitrile. ^c Lewis acidity, by FTIR of adsorbed d_3 -acetonitrile.

most one order higher. From these results it follows that Zn species in cationic form significantly support the aromatization reaction and that the selectivity to aromatics in n-hexane conversion is not a question of total conversion but the amount of Zn in the zeolite. The data obtained from TPDA (see Table I) shows that the introduction of zinc into cationic positions does not significantly changed the acidity of the catalysts in comparison with NH_4 -ZSM-5 zeolite. On the other hand, as shown in our previous work³⁰, the amount of ammonia desorbing over 450 °C from the catalyst increases with increasing Zn content in zeolite. This indicates that introduction of Zn into cationic positions causes acid-site strength redistribution and generation of new, relatively strong acid sites. FTIR data for NH_4 -ZSM-5 and 0.7 ZnZSM-5 catalysts (see Table I) as representatives of ion-exchanged ZnZSM-5 catalysts showed that by introduction of zinc into cationic positions, new Lewis acid sites are formed and the concentration of proton sites in the catalyst decreases (the excess over aluminium present in framework is caused probably by experimental error, but the absolute value has no effect on the evaluation of the results). This fact was also reflected in the results of toluene disproportionation, the reaction found to be sensitive to the Bronsted acidity in ZSM-5 zeolites (Table II). The results showed that the conversion of toluene on 0.7 ZnZSM-5 is twice lower in comparison with a pure NH_4 -ZSM-5 catalyst. But the amounts of toluene converted per hour and Bronsted site are over both zeolites practically the same indicating that the proton-site activity of zeolite does not change by introduction of Zn. So the decline of conversion on the 0.7 ZnZSM-5 catalyst reflects the decrease in proton-site number. The same can be stated from the results of n-hexane conversion at 350 °C (Table II). At that low temperature, only a

TABLE II

Activity of Broensted acid sites in the conversion of n-hexane (350 °C, 0.1 MPa) and disproportionation of toluene (380 °C, 0.1 MPa)

Catalyst	Total conversion, wt. %		Activity, mg hexane/ H^+ · h	
	n-hexane	toluene	n-hexane conversion	toluene conversion
NH_4 -ZSM-5	19.1	5.6	393	19
0.7 ZnZSM-5	7.4	2.7	372	22

small amount of aromatics was formed and the dominant reaction was n-hexane cracking. The total conversion on the 0.7 ZnZSM-5 catalyst was significantly lower in comparison with the $\text{NH}_4\text{-ZSM-5}$ catalyst indicating that at a low temperature, the total conversion reflects mainly the amount of Brønsted sites in zeolite. The amount of n-hexane converted on proton sites in both zeolites is practically the same.

From the results of these two test reactions it follows that the Brønsted acid-site strength in Zn-modified ZSM-5 catalysts is not influenced by the presence of Lewis acid sites. So the continuous increase in ammonia portion desorbed over 450 °C with increasing amount of Zn in $\text{NH}_4\text{-ZSM-5}$ indicates that the Zn^{2+} cations are relatively strong Lewis acid sites in ZnZSM-5 catalysts. At higher temperatures, these sites are responsible for the reactions leading to aromatics formation such as oligomerization of cracking products and dehydrogenation of cyclic intermediates (see the results of n-hexane conversion at 350 and 420 °C). The contribution of the thermal decomposition of n-hexane at 420 °C to the aromatics formation can be excluded on the basis of the result of n-hexane conversion on pure NaZSM-5. As can be seen from Table III, the conversion on NaZSM-5 was zero. From this it follows that neither 0.22 mmol of acid sites/g determined by TPDA (the acidity does not change even after multiple ion exchange with Na cations) in the NaZSM-5 catalyst, nor the reaction temperature initiate the n-hexane conversion. By introduction of Zn into cationic positions of NaZSM-5, the total conversion of n-hexane increases from zero on pure NaZSM-5 to 18.4 wt.% on NaZnZSM-5 catalyst (Table I). Generally, it

TABLE III
Characteristics of the mechanical-mixture catalysts

Catalyst	Zn mmol/g	Acidity ^a mmol/g	n-Hexane conversion ^b wt. %	Selectivity, %	
				aromatics	cracking products
ZnO-NH ₄ -ZSM-5	0.35	0.85	26.9	16.9	81.4
NaZSM-5	0	0.22	0	0	0
ZnO-NaZSM-5	0.35	0.37	0	0	0
Alumina	0	0	0	0	0
ZnO-alumina	0.35	0	0	0	0

^a By TPDA. ^b At 420 °C.

can be expected that in the ion exchange of sodium form of zeolites with the metal salt solutions, depending on pH of the solution, simultaneous ion exchange of proton for Na can proceed and Brønsted acid sites are formed. During the preparation of the NaZnZSM-5 catalyst, pH of the solution was not below 5.5 (measured at ambient temperature). Hence, at this low proton concentration in the solution, we do not assume the formation of Brønsted acid sites. The increased activity of practically inactive NaZSM-5 after Zn loading by ion exchange can be attributed to the ability of Zn cations as Lewis acid sites to initiate the formation of carbonium ions from n-hexane at higher temperatures.

For a better explanation of the function of Zn localization in ZSM-5 zeolites, ZnO-alumina and mechanical mixtures of ZnO with NH_4 -ZSM-5 or NaZSM-5 having the same Zn content as in the 0.7 ZnZSM-5 catalyst were prepared and tested in the aromatization of n-hexane at 420 °C (Table III).

The results show that the activity of ZnO–NaZSM-5 and ZnO-alumina catalysts in n-hexane conversion was zero (see Table III). From a comparison of the results obtained on the NaZnZSM-5 catalyst, where Zn was introduced by ion exchange (Table I), with the results on a mechanical mixture of ZnO and NaZSM-5 or alumina (Table III), it can be concluded that ZnO species alone at 420 °C are inactive in the n-hexane conversion. On the other hand, mechanical admixing of 0.35 mmol Zn^{2+}/g (as ZnO) to NH_4 -ZSM-5 decreases the total conversion from 42.4 wt.% on NH_4 -ZSM-5 to 26.9 wt.% on ZnO– NH_4 -ZSM-5. From a comparison of the activity/selectivity of the mechanical mixture ZnO– NH_4 -ZSM-5 with the results obtained on catalysts with different Zn contents in cationic positions (Table I), it can be seen that the activity/selectivity of the mechanical mixture ZnO and NH_4 -ZSM-5 roughly corresponds to the activity/selectivity of the 0.17 ZnZSM-5 ion-exchanged catalyst containing 0.09 mmol of zinc per gram in cationic positions. From TPDA results it can be seen (Fig. 1) that the amount of ammonia desorbing above 450 °C evidently increases on the mechanical mixture in comparison with NH_4 -ZSM-5, practically corresponding with the data on the 0.17 ZnZSM-5 catalyst. On the basis of the results we suggest that the changes in activity and selectivity of mechanical mixture of ZnO and NH_4 -ZSM-5 in comparison with pure ammonium forms of zeolite (NH_4 -ZSM-5) are caused by partial migration of Zn from ZnO into cationic positions by solid-state ion exchange during the activation of the catalyst at 450 °C before the experiments. We conclude that the ZnO species in extra-framework positions in ZSM-5 zeolite, in contrast to the statement of Kanai and Kawata¹⁹, are not active components of catalysts in aromatization of n-hexane and the amount and localization of Zn in

cationic positions of the zeolite is decisive for the activity/selectivity of the catalysts.

Differences between the results reported in the mentioned work¹⁹ and our results could be attributed to the fact that the catalytic tests reported by the authors were performed at higher temperature (500 °C) which alone can initiate conversion of n-hexane and that the mechanical mixtures were treated for 4 h at 550 °C before catalytic tests. Our preliminary study of mechanical mixtures of ZnO and NH₄-ZSM-5 indicates that the degree of solid-state ion exchange of Zn from ZnO into NH₄-ZSM-5 increases with increasing temperature and the time of thermal pre-treatment.

CONCLUSIONS

Introduction of zinc into cationic positions of NH₄-ZSM-5 zeolite causes acid-site strength redistribution and generation of new, relatively strong Lewis acid sites. Simultaneous presence of Lewis and Broensted acid sites in ZSM-5 zeolite does not affect the strength of Broensted acid sites in zeolite.

For activity/selectivity of aromatization of n-hexane in Zn-modified ZSM-5 zeolites, the amount and localization of Zn in cationic positions are decisive. The reaction of n-hexane can be also initiated by the Zn species alone in cationic positions of the zeolite. ZnO species alone as an ex-

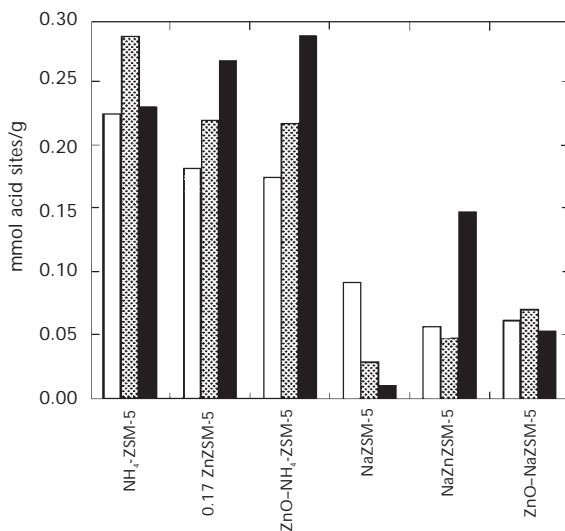


FIG. 1

Amount of ammonia desorbed in the temperature range: □ 350–400 °C, ▨ 400–450 °C, ■ 450–550 °C

tra-framework phase was found to be an inactive component in the catalyst for aromatization of n-hexane. The influence of ZnO on the performance of pure ammonium forms of ZSM-5 zeolite in n-hexane conversion is a result of partial migration of zinc into cationic positions of zeolite by solid-state ion exchange.

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