

INTERACTION OF ZnO WITH ZSM-5 ZEOLITESEdita ROJASOVÁ^{1,*}, Agáta SMIEŠKOVÁ², Pavol HUDEC³ and Zdenek ŽIDEK⁴*Department of Petroleum Technology and Petrochemistry, Faculty of Chemical Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic;**e-mail: ¹ rojasova@chelin.chtf.stuba.sk, ² smiesko@chelin.chtf.stuba.sk,**³ phudec@chelin.chtf.stuba.sk, ⁴ zidek@checdek.stuba.sk*

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Dedicated to Professor Ludovít Treindl on the occasion of his 70th birthday.

The possibility of introduction of zinc from ZnO into cationic positions of H- and NH₄-ZSM-5 zeolites by solid-state ion exchange was investigated. It was concluded that during thermal pretreatment of a mechanical mixture of ZnO with acid forms of ZSM-5 zeolite, introduction of Zn species into cationic positions as a consequence of the proposed solid-state ion exchange proceeds, but its degree is limited. It indicates that the extent of interaction of Zn species is probably controlled by the concentration of cationic sites on the external surface of the zeolite.

Key words: Solid-state ion exchange; Zinc oxide; Zn-ZSM-5; Zeolites; Heterogeneous catalysis.

It has been reported that mechanical mixtures of ZnO with acid forms of ZSM-5 zeolites are highly active and selective in aromatization of lower alkanes¹⁻³. The role and the state of metallic species in the mechanical mixtures under the reaction conditions have also been the subject of a wide discussion²⁻⁸.

Kanai and Kawata² have reported that a mechanical mixture of ZnO and NH₄-ZSM-5 is a bifunctional catalyst in which ZnO in the n-hexane aromatization catalyzes dehydrogenation of n-hexane into hexene and of the oligomerized products into aromatics.

On the other hand, in our previous work⁹ it was observed that both mechanical mixtures of ZnO with alumina and sodium form of ZSM-5 were totally inactive in n-hexane conversion at 420 °C, indicating that ZnO as an extra-framework phase is not able to activate n-hexane under these conditions. We have only observed an increased selectivity to aromatics on a mechanical mixture ZnO + NH₄-ZSM-5 as compared with NH₄-ZSM-5. We have explained this fact by partial migration of Zn from ZnO into cationic positions due to solid-state ion exchange during thermal pretreatment of the mechanical mixture before measurement.

Discrepancies between our statement and the statement reported by Kanai and Kawata² concerning the activity of ZnO species could be caused by different reaction and pretreatment conditions of the catalyst (n-hexane conversion was in that work performed at 500 °C, at which a contribution of thermal decomposition of n-hexane to the conversion cannot be excluded, and the mechanical mixture of ZnO with NH₄-ZSM-5 was before testing pretreated at 550 °C for 4 h, in our case⁹ just 1 h at 450 °C).

We have also reported⁹ that for activity/selectivity of Zn-modified ZSM-5 zeolites, Zn²⁺ species in cationic positions, relatively strong Lewis acid sites, are decisive. By temperature-programmed desorption of ammonia (TPDA) it was also shown that with increasing amount of zinc in cationic positions, the amount of ammonia desorbed above 450 °C increases and the n-hexane conversion at 420 °C continuously increases with simultaneous increase in the selectivity to aromatics. In addition, it was shown that the toluene conversion continuously decreases with increasing amount of zinc in cationic positions, indicating a decrease in the concentration of Brønsted acid sites in the zeolite¹⁰.

Based on these conclusions, the aim of this work was to investigate the possibility of introduction of zinc from ZnO into cationic positions of ZSM-5 zeolite by solid-state ion exchange (SSIE) in dependence of the pretreatment temperature and time and ZnO concentration in the mechanical mixture.

EXPERIMENTAL

The NaZSM-5 zeolite was supplied by Slovnaft Research Institute of Petroleum and Hydrocarbon Gases, Inc. Bratislava (Si/Al = 14, 1.01 mmol Al/g). Acid forms of ZSM-5 zeolites were prepared from NaZSM-5 zeolite by ion exchange with 0.5 M HCl (H-ZSM-5) and with 1 M NH₄NO₃ (NH₄-ZSM-5).

ZnZSM-5 catalysts with different amounts of zinc were prepared by ion exchange of NH₄-ZSM-5 with aqueous solution of zinc acetate (for details, see ref.⁹).

Mechanical mixtures of ZnO with acid forms of ZSM-5 zeolite were prepared by mixing 0.085, 0.2, 0.23, 0.27, 0.35 and 0.5 mmol Zn/g of catalyst as ZnO with H-ZSM-5 (ZnO + H-ZSM-5) and NH₄-ZSM-5 (ZnO + NH₄-ZSM-5). Before measurements, the mechanical mixtures were pretreated *in situ* in a stream of dry air at 450, 500 or 550 °C for 1, 3, 5 and 11.5 h, respectively.

The acidity of the thermally pretreated samples was determined by TPDA. Adsorption of ammonia was carried out at 220 °C. Before adsorption, the samples were activated *in situ* at 500 °C for 1 h in a stream of helium. The amount of desorbed ammonia in the ranges 220–300, 300–350, 350–400, 400–450 and 450–550 °C was detected by titration of an excess of 0.05 M H₂SO₄ with 0.05 M solution of NaOH.

Conversion of n-hexane and disproportionation of toluene, as test reactions, were performed in the vapour phase, with 100 mg of catalyst in a continuous glass flow microreactor

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 tests, thermally pretreated samples were activated in a stream of dry air (50 ml/min) at 450 °C for 1 h. Conversion of n-hexane was carried out at 420 °C. Toluene disproportionation was performed at 380 °C.

The reaction products were analyzed by gas chromatography using a HP-1 capillary column (15 m × 0.530 mm) and FID detector.

RESULTS AND DISCUSSION

The influence of the pretreatment time and temperature on the acidity and activity in model reactions was investigated on a mechanical mixture ZnO + H-ZSM-5 containing 0.35 mmol Zn/g of catalyst. The results of TPDA are given in Fig. 1. As it can be seen from this figure, time and temperature of pretreatment of the mechanical mixture have no significant influence on the total acidity of the samples. However, the amount of ammonia desorbed above 450 °C increases with the pretreatment time, reaching a maximum on mechanical mixture treated for 3 h. As compared with the pure acid form of ZSM-5, the amount of ammonia desorbed above 450 °C from mechanical mixtures was higher. Also it can be seen that the pretreatment temperature in the range 450–550 °C and the time exceeding 3 h have no effect on the amount of ammonia desorbing above 450 °C.

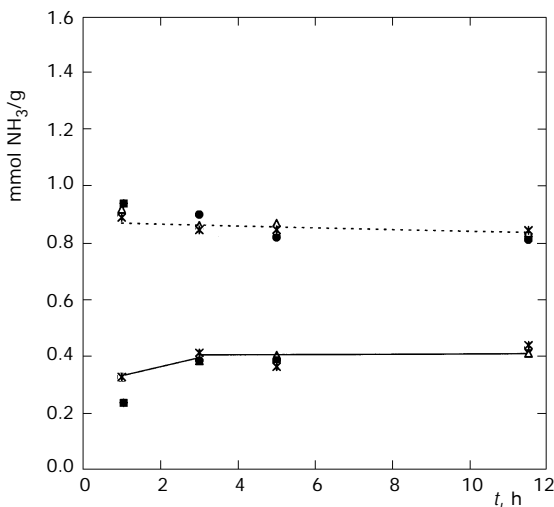


FIG. 1

Acidity of the ZSM-5 catalysts in dependence on the pretreatment time (t): ■ H-ZSM-5; mechanical mixture ZnO + H-ZSM-5 (0.35 mmol Zn/g) pretreated at ● 450 °C, Δ 500 °C, * 550 °C. - - - Total acidity, — NH₃ desorbed above 450 °C

The results of toluene disproportionation, the reaction was found to be sensitive to the Brønsted acidity in ZSM-5 zeolites, obtained on mechanical mixtures ZnO + H-ZSM-5 are presented in Fig. 2. Because the values of toluene conversion over all tested catalysts decreased with contact time, activities of the catalysts were compared on the basis of initial conversion calculated from linear dependence of $\ln(\text{conversion}) = f(\ln(\text{time}))$ extrapolating to $\ln(\text{time}) = 0$.

As can be seen (Fig. 2), the activity of mechanical mixtures is lower compared to the pure acid form of ZSM-5. We can also observe that the activity slightly decreases with the pretreatment time but, as can be seen on mechanical mixtures, neither pretreatment temperature in the range 450–550 °C nor the time exceeding 3 h has any influence on the activity of the samples. The observed decrease in the activity of the mechanical mixture in comparison with the pure acid form can be an indirect evidence that the concentration of proton sites in the mechanical mixtures decreases. This can be supposed on the basis of the results reported in our previous work¹⁰, where it was shown that increasing the ion-exchange degree the conversion of toluene in ion-exchanged Zn-ZSM-5 samples continuously decreases. In addition on the basis of FTIR measurements using d_3 -acetonitrile as a probe molecule it was proved that introduction of zinc

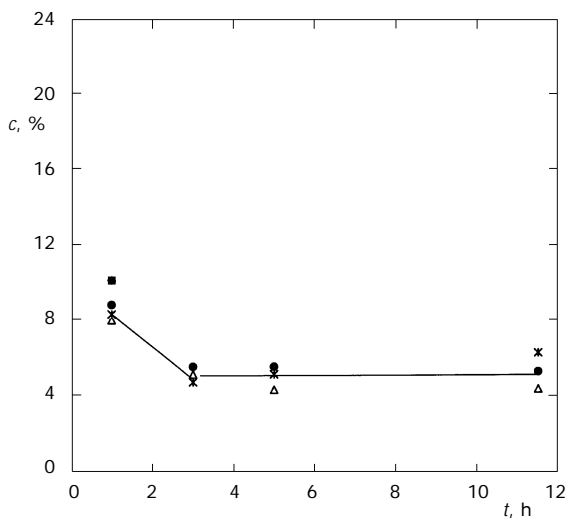


FIG. 2

Toluene conversion (c) (380 °C, 0.1 MPa) in dependence on the pretreatment time (t): ■ over H-ZSM-5; over mechanical mixture ZnO + H-ZSM-5 (0.35 mmol/g) pretreated at ● 450 °C, Δ 500 °C, * 550 °C

into cationic positions of ZSM-5 zeolites causes decrease in the concentration of proton sites in the catalyst and generation of new, relatively strong Lewis acid sites⁹.

n-Hexane conversion at 420 °C was used as a test reaction for aromatization activity/selectivity of the mechanical mixtures. Activity of all tested catalysts in n-hexane conversion was stable and did not change with contact time, catalysts are compared on the basis of average values of conversion (Fig. 3). It can be observed that thermal activation of the mechanical mixture changes the catalyst activity/selectivity as compared with the pure acid form of ZSM-5 but, again, activation exceeding 3 h has no further effect on the catalyst performance. Likewise, as it was observed in toluene conversion and in TPDA measurements, pretreatment temperature of the mechanical mixture in the range 450–550 °C has no noticeable effect in this case on the aromatization activity/selectivity of the samples.

In our previous work⁹ it was shown that ZnO as an extra-framework phase is not able to activate n-hexane under given conditions (420 °C). The presented activity/selectivity in the test reactions and TPDA data of thermally treated mechanical mixture ZnO + H-ZSM-5 are different from those of pure acid ZSM-5 zeolite. We regard this fact as an indirect evidence that during activation of the mechanical mixture some interaction of ZnO with

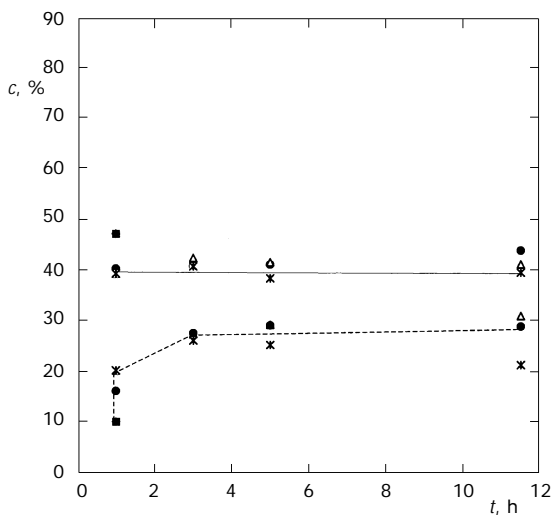


FIG. 3

Conversion of n-hexane (*c*) (420 °C, 0.1 MPa) in dependence on the pretreatment time (*t*): ■ over H-ZSM-5; over mechanical mixture ZnO + H-ZSM-5 (0.35 mmol/g) pretreated at ● 450 °C, ▲ 500 °C, * 550 °C. — Total conversion, - - - selectivity to aromatics

the zeolite framework proceeds, probably *via* SSIE. The results showed that after 3 h activation of a sample containing 0.35 mmol Zn/g, some “steady” state in this proposed interaction was reached, independently of a temperature in the range 450–550 °C.

On the basis of these results, mechanical mixtures of ZnO with NH_4 -ZSM-5 containing different amounts of ZnO (0.085–0.5 mmol Zn/g) were prepared and pretreated at 450 °C for 3 h. The results of TPDA measurements of these samples are presented in Fig. 4. As it was mentioned above, it was shown in our previous work¹⁰ that increasing continuously the amount of Zn in cationic positions, the amount of ammonia desorbed above 450 °C determined by TPDA increases at virtually the same total acidity of the samples. As can be seen in Fig. 4, the amount of ammonia desorbing over 450 °C in the mechanical mixtures is higher compared to the pure acid form of ZSM-5 zeolite but reaches a maximum in the mechanical mixture containing 0.085 mmol Zn/g. Then, independently of the increasing amount of ZnO in the mixture, it remains constant.

The same trend was observed in the toluene conversion (Fig. 5). As it was shown in our previous work¹⁰, increasing the Zn concentration in cationic positions, the toluene conversion continuously decreases. With the mechanical mixtures, the toluene conversion on a sample containing 0.085 mmol Zn/g decreases in comparison with the pure acid form of ZSM-5 but then it does not change with increasing amount of ZnO in the mixture (Fig. 5).

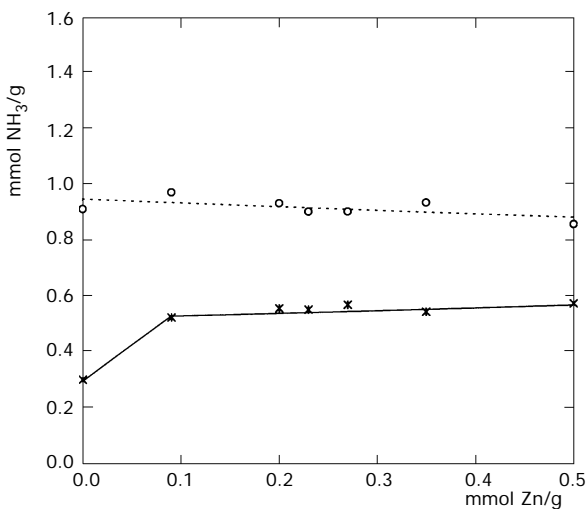


FIG. 4

Acidity of mechanical mixtures ZnO + NH_4 -ZSM-5 pretreated at 450 °C for 3 h in dependence on ZnO concentration: ○ total acidity, * NH_3 desorbed above 450 °C

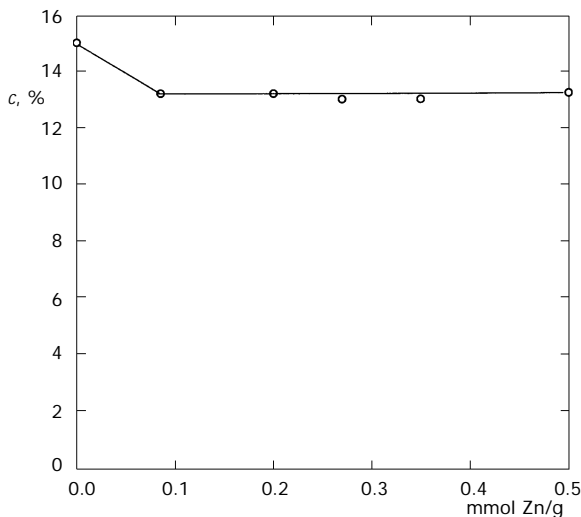


FIG. 5
Toluene conversion (c) (380 °C, 0.1 MPa) over mechanical mixtures ZnO + NH₄-ZSM-5 (pretreated at 450 °C for 3 h) in dependence on ZnO concentration

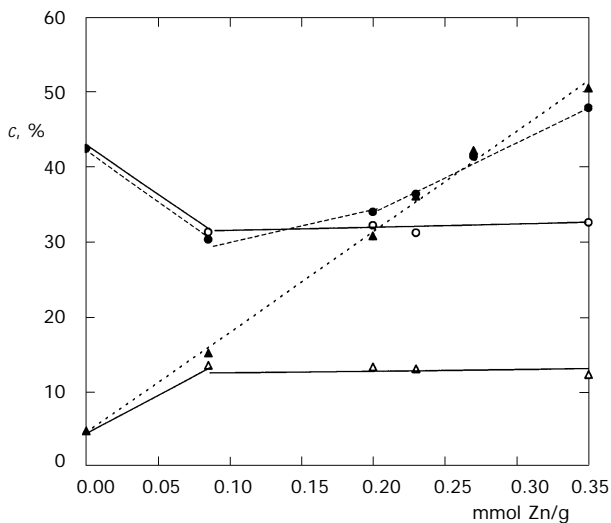


FIG. 6
Conversion of n-hexane (c) (420 °C, 0.1 MPa); over mechanical mixtures ZnO + NH₄-ZSM-5 pretreated at 450 °C for 3 h: ○ conversion, Δ selectivity to aromatics; - - - over ion-exchanged Zn-ZSM-5 samples: ● conversion, ▲ selectivity to aromatics

Figure 6 presents the dependence of selectivity and activity in n-hexane aromatization on the Zn amount for a series of ion-exchanged samples and for the mechanical mixtures pretreated at 450 °C for 3 h.

From comparison of the results obtained with the mentioned two series of samples, it can be seen that in the n-hexane conversion, the mechanical mixtures ZnO + NH₄-ZSM-5 containing different amounts of ZnO (0.085–0.5 mmol Zn/g of catalyst) reached the activity/selectivity (independently on the ZnO concentration) of the ion-exchanged sample with 0.085 mmol Zn/g. Hence it can be assumed that the maximum degree of the ZnO interaction (probably *via* SSIE) is roughly 17%.

The presented results confirmed the assumption from our previous work⁹ that during thermal activation of mechanical mixtures ZnO + NH₄-ZSM-5 some interaction of Zn species with zeolite cationic positions proceeds. In addition, the broadened presented results enlarged the information concerning the influence of the pretreatment time and temperature on the process.

The results showed that the degree of interaction of Zn species from ZnO with zeolite is limited, the temperature of thermal treatment (450–550 °C) has a marginal effect, and the system reaches an “equilibrium” state after 3 h of thermal activation. A possible explanation for the limited interaction of Zn species from ZnO with cationic positions of ZSM-5 could be that the proposed SSIE is controlled by zeolite, probably by the amount of ion-exchange sites on the zeolite external surface. However, to elucidate this phenomena, a more detailed study is necessary. The present study confirmed the assumption that ZnO as an extra-framework phase in acid ZSM-5 is, under given conditions, inactive in n-hexane aromatization because the activity and selectivity in the mentioned reaction remains constant in spite of increasing concentration of ZnO in zeolite. Thus ZnO as an extra-framework phase does not contribute to the catalyst performance.

CONCLUSIONS

In this work it was indirectly proven that the interaction of some Zn species with the acid forms of ZSM-5 zeolite during thermal pretreatment of the mechanical mixture proceeds. A possibility of zinc introduction into cationic positions was proposed as a consequence of SSIE between ZnO and H and NH₄ forms of ZSM-5 zeolite. The proposed SSIE is limited and proceeds to a relatively very low degree. Our preliminary hypothesis is that the extent of interaction of Zn species is probably controlled by the concentra-

tion of cationic sites on the external surface of the zeolite. However, to elucidate this phenomena, a more detailed study is necessary.

It was also shown that while the results obtained with mechanical mixtures are different from those obtained over the pure acid form of ZSM-5 zeolite, the amount of ZnO in the mechanical mixture (in the range 0.085–0.5 mmol Zn/g of catalyst) has no influence on the ammonia portion desorbed above 450 °C, on the toluene conversion and on the activity/selectivity in the n-hexane conversion. These results confirm our presumption⁹ that ZnO as an extra-framework phase is an inactive component of the catalyst in the n-hexane aromatization.

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