

# Reactivity of Propene, *n*-Butene, and Isobutene in the Hydrogen Transfer Steps of *n*-Hexane Cracking over Zeolites of Different Structure

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The reaction of *n*-hexane cracking over HZSM-5, HY zeolite and mordenite (HM) was studied in accordance with the procedure of the  $\beta$ -test recently proposed for quantitative characterization of zeolite hydrogen transfer activity. It is shown that this procedure allows one to obtain quantitative data on propene, *n*-butene, and isobutene reactivities in the hydrogen transfer steps of the reaction. The results demonstrate that in the absence of steric constraints (large pore HY and HM zeolites) isobutene is approximately 5 times more reactive in hydrogen transfer than *n*-butene. The latter, in turn, is about 1.3 times more reactive than propene. With medium pore HZSM-5, steric inhibition of the hydrogen transfer between *n*-hexane and isobutene is observed. This results in a sharp decrease in the isobutene reactivity: over HZSM-5 zeolites isobutene is only 1.2 times more reactive in hydrogen transfer than *n*-butene. On the basis of these data it is concluded that the  $\beta$ -test measures the "real" hydrogen transfer activity of zeolites, i.e., the activity that summarizes the effects of the acidic and structural properties of zeolites. An attempt is made to estimate the "ideal" zeolite hydrogen transfer activity, i.e., the activity determined by the zeolite acidic properties only. The estimations obtained show that this activity is approximately 1.8 and 1.6 times higher for HM zeolite in comparison with HZSM-5 and HY zeolites, respectively. © 1994 Academic Press, Inc.

## INTRODUCTION

Hydrogen transfer between light olefins, on the one hand, and paraffins or naphthenes, on the other hand, plays an important role in many reactions catalyzed by zeolites, such as paraffin cracking, paraffin and olefin aromatization, methanol to hydrocarbon conversion, and paraffin alkylation with olefins (1). Although there are a great number of publications on these reactions, only a few quantitative data on the reactivity of different olefins

in hydrogen transfer reactions are available (2, 3). It should be noted that these data cannot be easily reproduced, since the authors of the papers (2, 3) have used complex kinetic models.

Recently a test method ( $\beta$ -test) for quantitative characterization of the zeolite hydrogen transfer activity was proposed (4), based on the determination of the rate of isobutane formation during *n*-hexane cracking reaction at 400°C. In this paper we demonstrate that the experimental procedure of the  $\beta$ -test allows one to obtain quantitative data on the reactivity of C<sub>3</sub><sup>=</sup>–C<sub>4</sub><sup>=</sup> olefins in the hydrogen transfer steps of the *n*-hexane cracking reaction. We also compare propene, *n*-butene, and isobutene reactivities determined for the zeolites of different pore structure.

## EXPERIMENTAL

Two parent HZSM-5 zeolites with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 34 and 240 (samples defined as Z-34 and Z-240, respectively), Y zeolite (sample HY, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.8), and mordenite (sample HM, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 15) were used in this study. Another sample, defined as Z-34ST, was obtained by steaming the ammonium form of ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 34) with pure water vapour at 400°C for 2 h. Details of catalyst preparation are reported elsewhere (5).

The *n*-hexane cracking reaction was carried out at 400°C according to the procedure of the  $\beta$ -test (4). The GC analysis of the reaction products was done on line at a time-on-stream of 7 min for HY and all HZSM-5 catalysts. As is clear from Fig. 1, the experimental data obtained in this way characterize the catalytic properties of the fresh zeolites under stationary conditions of the reaction. We observed relatively rapid deactivation of HM catalyst (see Fig. 1). Therefore, in order to obtain data corresponding to the initial activity of this catalyst, the GC analysis was done at a time-on-stream of 1 min. The  $\alpha$ -activity test was performed over all samples at 538°C according to the procedure described by Olson *et al.* (6).

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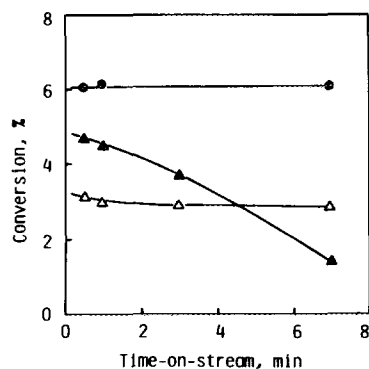
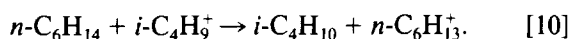
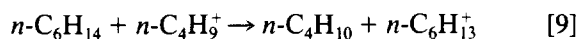
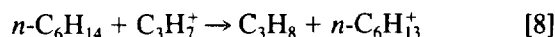
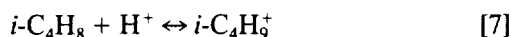
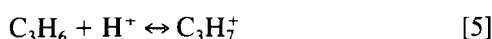
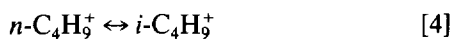
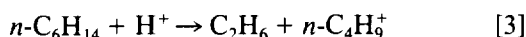
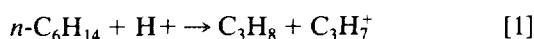


FIG. 1. Effect of time-on-stream on the conversion of *n*-hexane over Z-34 (●), HY (△), and HM (▲) catalysts.

## RESULTS AND DISCUSSION

### Theory

In accordance with the mechanism of paraffin cracking over zeolites (7, 8), propane and *n*-butane are formed (see reaction scheme shown below) in the *n*-hexane protolytic cracking steps proceeding via formation of a nonclassical penta-coordinated carbonium ion ( $n\text{-C}_6\text{H}_{15}^+$ ) as the reaction transition state, and in the steps of hydride transfer from *n*-hexane to secondary propyl ( $\text{C}_3\text{H}_7^+$ ) and butyl ( $n\text{-C}_4\text{H}_9^+$ ) carbenium ions, respectively. Isobutane is formed only in the steps of hydride transfer from *n*-hexane to tert-butyl carbenium ion ( $i\text{-C}_4\text{H}_9^+$ ). The latter is produced by isomerization of the secondary butyl carbenium ion which proceeds rapidly in comparison with the steps of *n*-hexane transformation (7). The secondary butyl carbenium ion, in turn, is the primary product of the *n*-hexane protolytic cracking steps, i.e.,



The reaction scheme shown above results in the following equations for the rates of propane, *n*-butane, and iso-

butane formation:

$$R(\text{C}_3) = k_{\text{CR1}}[\text{C}_6][\text{Z}] + k_{\text{HT1}}[\text{C}_6][\text{C}_3^-\text{Z}] \quad [11]$$

$$R(n\text{C}_4) = k_{\text{CR2}}[\text{C}_6][\text{Z}] + k_{\text{HT2}}[\text{C}_6][n\text{C}_4^-\text{Z}] \quad [12]$$

$$R(i\text{C}_4) = k_{\text{HT3}}[\text{C}_6][i\text{C}_4^-\text{Z}] \quad [13]$$

Here  $k_{\text{CR1}}$  and  $k_{\text{CR2}}$  are the rate constants for reaction steps [1] and [2], respectively;  $k_{\text{HT1}}$ ,  $k_{\text{HT2}}$ , and  $k_{\text{HT3}}$  are the rate constants for reaction steps [8], [9], and [10], respectively;  $[\text{C}_6]$  is the concentration of *n*-hexane in the reaction mixture;  $[\text{Z}]$  is the concentration of the vacant acid sites;  $[\text{C}_3^-\text{Z}]$ ,  $[n\text{C}_4^-\text{Z}]$  and  $[i\text{C}_4^-\text{Z}]$  are the concentrations of propyl, secondary butyl, and tertiary butyl carbenium ions, respectively.

Assuming a rapid equilibrium between carbenium ions and olefins, one can transform Eqs. [11]–[13] into

$$R(\text{C}_3) = k_{\text{CR1}}[\text{C}_6][\text{Z}] + k_{\text{HT1}}K_{a1}[\text{C}_6][\text{C}_3^-\text{Z}] \quad [14]$$

$$R(n\text{C}_4) = k_{\text{CR2}}[\text{C}_6][\text{Z}] + k_{\text{HT2}}K_{a2}[\text{C}_6][n\text{C}_4^-\text{Z}] \quad [15]$$

$$R(i\text{C}_4) = k_{\text{HT3}}K_{a3}[\text{C}_6][i\text{C}_4^-\text{Z}] \quad [16]$$

where  $K_{a1}$ ,  $K_{a2}$ , and  $K_{a3}$  are the adsorption constants for propene, *n*-butene, and isobutene, respectively (see reaction steps [5]–[7]);  $[\text{C}_3^-]$ ,  $[n\text{C}_4^-]$ , and  $[i\text{C}_4^-]$  are the concentrations of propene, *n*-butene, and isobutene, respectively.

At low *n*-hexane conversions olefin concentration is low, and only a small fraction of acid sites is occupied by olefins. Therefore, it can be assumed that  $[\text{Z}] \approx 1$ , and Eqs. [14]–[16] can be simplified to

$$R(\text{C}_3) = k_{\text{CR1}}[\text{C}_6] + k_{\text{HT1}}^*[\text{C}_6][\text{C}_3^-] \quad [17]$$

$$R(n\text{C}_4) = k_{\text{CR2}}[\text{C}_6] + k_{\text{HT2}}^*[\text{C}_6][n\text{C}_4^-] \quad [18]$$

$$R(i\text{C}_4) = k_{\text{HT3}}^*[\text{C}_6][i\text{C}_4^-] \quad [19]$$

where  $k_{\text{HT1}}^* = k_{\text{HT1}}K_{a1}$ ,  $k_{\text{HT2}}^* = k_{\text{HT2}}K_{a2}$ , and  $k_{\text{HT3}}^* = k_{\text{HT3}}K_{a3}$ . Rate constants  $k_{\text{HT1}}^*$ ,  $k_{\text{HT2}}^*$ , and  $k_{\text{HT3}}^*$  can be used for quantitative characterization of propene, *n*-butene, and isobutene reactivities in the hydrogen transfer steps of the *n*-hexane cracking reaction.

### Reactivity of $\text{C}_3^-$ - $\text{C}_4^-$ Olefins in Hydrogen Transfer

Figures 2A, 3A, and 4A show the effect of *n*-hexane conversion on the rates of propane, *n*-butane, and isobutane formation. In accordance with the mechanism of formation of these paraffins, one can conclude that propane and *n*-butane formation rates extrapolated to zero *n*-hexane conversion are equal to the rates of propane

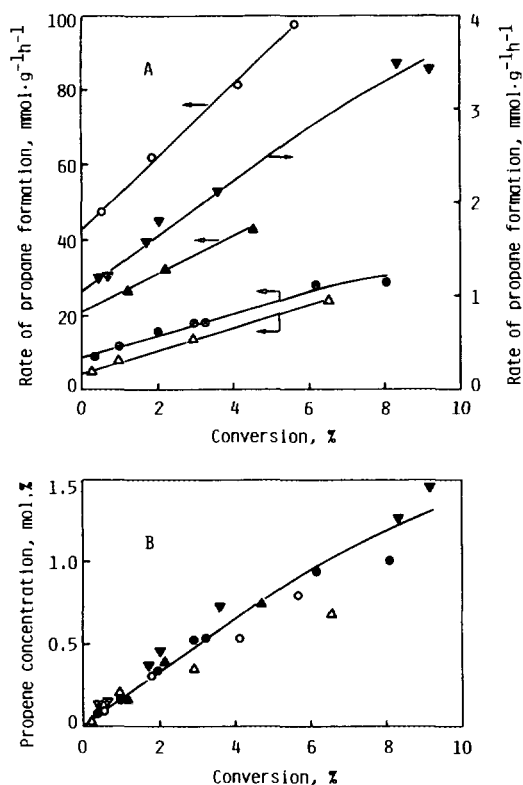


FIG. 2. Effect of *n*-hexane conversion on the rate of propane formation (A) and on the propene concentration (B). Catalysts: Z-34 (●); Z-34ST (○); Z-240 (▼); HY (△); HM (▲).

and *n*-butane formation in the steps of *n*-hexane protolytic cracking. The isobutane formation rate determined at zero *n*-hexane conversion, in agreement with the reaction mechanism, is equal to zero.

Figures 2B, 3B, and 4B demonstrate that an increase in *n*-hexane conversion is followed by a linear increase in the concentrations of the product olefins: propene, *n*-butene, and isobutene. These olefins interact with *n*-hexane by the hydrogen transfer mechanisms and produce, in this way, propane, *n*-butane, and isobutane. As a consequence of this, the rates of formation of C<sub>3</sub>-C<sub>4</sub> paraffins increase with increasing conversion of *n*-hexane (see Figures 2A, 3A, and 4A).

At low *n*-hexane conversions (below 4–5%), when the concentration of *n*-hexane is approximately constant, the rates of the protolytic cracking steps can be considered as constants. Hence, the rates of propane and *n*-butane formation in the hydrogen transfer steps ( $R_{HT}(C_3)$  and  $R_{HT}(nC_4)$ , respectively) can be determined as the difference between the total rates of propane and *n*-butane formation ( $R(C_3)$  and  $R(nC_4)$ , respectively), directly observed in the experiments, and the rates of propane and *n*-butane formation in the protolytic cracking steps ( $R_{CR}^o(C_3)$  and  $R_{CR}^o(nC_4)$ , respectively), determined at

zero *n*-hexane conversion, i.e.,

$$R_{HT}(C_3) = R(C_3) - R_{CR}^o(C_3) = k_{HT1}^*[C_6][C_3^-] \quad [20]$$

$$R_{HT}(nC_4) = R(nC_4) - R_{CR}^o(nC_4) = k_{HT2}^*[C_6][nC_4^-]. \quad [21]$$

From Eqs. [20] and [21], as well as from Eq. [19], it follows that the ratio between the rate of propane (*n*-butane and isobutane) formation in the hydrogen transfer steps and the concentration of propene (*n*-butene and isobutene, respectively) is proportional to  $k_{HT1}^*$  ( $k_{HT2}^*$  and  $k_{HT3}^*$ , respectively) and should be constant. Experimental data shown in Figs. 2–4 demonstrate that both the rate of the product paraffin formation in the hydrogen transfer steps and the concentration of the corresponding olefin are strictly proportional to *n*-hexane conversion (at conversions below 4%). Hence, the ratio between them is constant and can be used for quantitative characterization of the olefin reactivity in the hydrogen transfer steps of *n*-hexane cracking.

Table 1 contains estimations of C<sub>3</sub><sup>-</sup>-C<sub>4</sub><sup>-</sup> olefin reactivities obtained on the basis of the experimental data shown in Figs. 2–4. The presented data demonstrate that over all

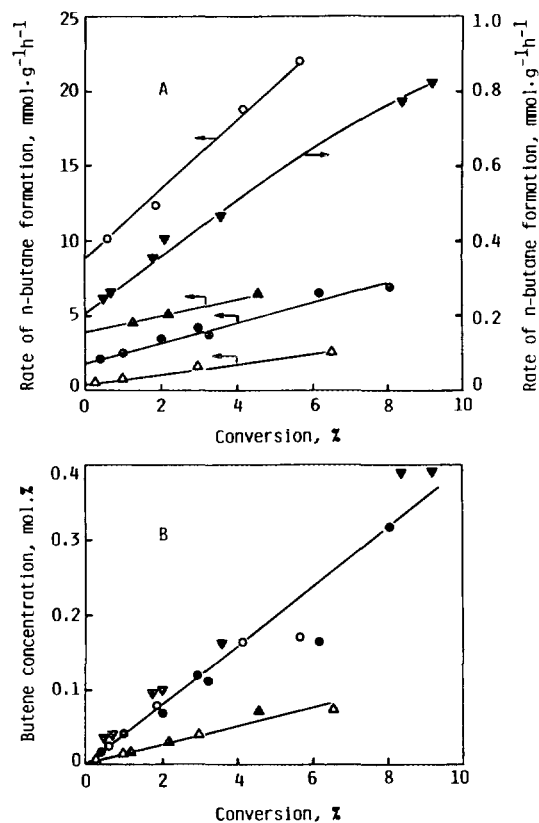


FIG. 3. Effect of *n*-hexane conversion on the rate of *n*-butane formation (A) and on the *n*-butene concentration (B). Catalysts: Z-34 (●); Z-34ST (○); Z-240 (▼); HY (△); HM (▲).

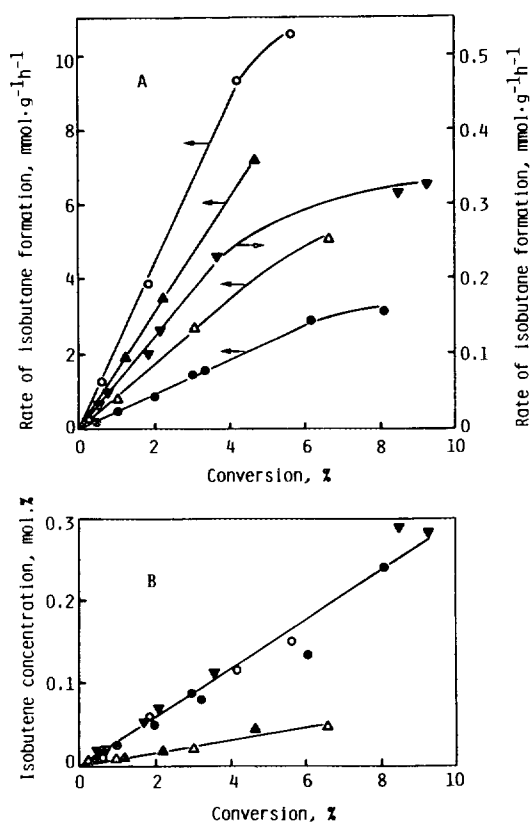


FIG. 4. Effect of *n*-hexane conversion on the rate of isobutane formation (A) and on the isobutene concentration (B). Catalysts: Z-34 (●); Z-34ST (○); Z-240 (▼); HY (△); HM (▲).

three HZSM-5 zeolites, *n*-butene is slightly more reactive than propene. The difference between *n*-butene and propene reactivities increases when the reaction of *n*-hexane cracking takes place on HY and HM zeolites, but again this difference is not large. From Table 1 it follows that isobutene is the most reactive olefin. With HZSM-5 cata-

TABLE 1

Propene, *n*-Butene, and Isobutene Reactivities in the Hydrogen Transfer Steps of *n*-Hexane Cracking over Different Zeolites

Catalyst	Olefin reactivity <sup>a</sup>		
	Propene	<i>n</i> -Butene	Isobutene
Z-34	1	1.13	1.18
Z-34ST	1	1.18	1.61
Z-240	1	1.15	1.40
HZSM-5 (average)	1	1.15	1.40
HY	1	1.37	6.20
HM	1	1.33	6.71

<sup>a</sup> Reactivity of propene ( $R_{HT}(C_3)/[C_3^+]$ ) has been taken as unity for each catalyst.

lysts, the difference in isobutene and *n*-butene reactivities is not large (1.2 times), but in the case of HY and HM catalysts, isobutene is approximately 5 times more reactive than *n*-butene.

It is worthwhile to mention that the kinetic modeling studies of *n*-hexane cracking over HZSM-5 have shown (3) that the ratio between the reactivities of C<sub>4</sub><sup>-</sup> olefins (*n*-butene and isobutene were treated together) and propene in the hydrogen transfer steps is about 1.5. This estimation is in reasonable agreement with the estimations obtained in this work (see Table 1).

The difference in the reactivities of propene, *n*-butene, and isobutene observed with the large pore HY and HM zeolites can be explained if we take into consideration the properties of carbenium ions (9) generated by these olefins. Isobutene generates the tert-butyl carbenium ion which is much more stable than the secondary butyl carbenium ion generated by *n*-butene. The latter, in turn, is more stable than the secondary propyl carbenium ion produced by propene. The difference in carbenium ion stabilities results (i) in the difference in carbenium ion concentrations (different adsorption constants  $K_{a1}$ ,  $K_{a2}$ , and  $K_{a3}$ ) and (ii) in the difference in carbenium ion reactivities (different rate constants  $k_{HT1}$ ,  $k_{HT2}$ , and  $k_{HT3}$ ). It may be assumed that the more stable tertiary carbenium ion is less reactive than the secondary carbenium ion. In this case, having in mind the data of Table 1 which characterize the resultant effect of carbenium ion concentration and reactivity factors, we come to the conclusion that the carbenium ion concentration factor is more important for olefin reactions than the carbenium ion reactivity factor. It seems probable that the counteraction of these two factors is the reason for the not-so-large difference in the observed propene, *n*-butene, and isobutene reactivities as one might have expected taking into consideration only the difference in stabilities (and, consequently, concentrations) of carbenium ions generated by these olefins.

Table 1 shows that the difference in the *n*-butene and isobutene reactivities decreases sharply in the case when the reaction of *n*-hexane cracking is carried out over medium pore HZSM-5 zeolites. This result can be easily understood. It is well known that hydrogen transfer reactions proceed via sterically large bimolecular transition state (1). According to Haag *et al.* (10), the cross section of the hydrogen transfer transition state is  $4.9 \times 6 \text{ \AA}^2$  for the reaction between secondary carbenium ion and *n*-hexane (two secondary carbon atoms are involved in the reaction). For reaction between secondary carbenium ion and 3-methylpentane (secondary and tertiary carbon atoms are involved in the reaction) the cross section of the transition state is  $6 \times 7 \text{ \AA}^2$  (10). In our case, a hydride ion is abstracted from the secondary carbon atom in the *n*-hexane molecule by the secondary and tertiary butyl

carbenium ions. In the latter case the cross section of the transition state should be the same as in the case of 3-methylpentane reaction with the secondary carbenium ion. This means that the reaction between *n*-hexane and tert-butyl carbenium ions should be strongly constrained in HZSM-5, since the cross section of the ZSM-5 channels is  $5.3 \times 5.6 \text{ \AA}^2$  (11). It should be noted that hydrogen transfer between *n*-hexane and the secondary propyl and butyl carbenium ions can be also sterically restricted in HZSM-5. However, it is clear that in this case steric restriction will be less important than in the case of the tert-butyl carbenium ion reaction.

Thus, we are coming to the conclusion that the small difference in the isobutene and *n*-butene hydrogen transfer reactivities, directly observed in our experiments, is due to the transition-state selectivity phenomena in hydrogen transfer reactions in zeolites. The existence of these phenomena was neatly predicted by Haag *et al.* (10) on the basis of the comparison of *n*-hexane and 3-methylpentane cracking rates observed over medium pore HZSM-5 and large pore HY zeolites. Further work to ascertain the role of steric constraints in the hydrogen transfer between *n*-hexane and secondary carbenium ions over HZSM-5 is in progress.

#### Zeolite Hydrogen Transfer Activity

As mentioned above, the experimental data of this work were obtained in accordance with the procedure of the  $\beta$ -test recently proposed (4) for quantitative characterization of zeolite hydrogen transfer activity. In this test zeolite activity is characterized by the ratio between the rate of isobutane formation and the concentration of isobutene. In view of the results presented above it is clear that the  $\beta$ -test measures the "real" zeolite hydrogen transfer activity, i.e., the activity that summarizes the effects of the acidic and structural properties of the zeolites. In contrast with this, the ratio between the propane formation rate in the hydrogen transfer reaction steps and the propene concentration can be used for characterization of the zeolite hydrogen transfer activity that depends mainly on the acidic properties of the zeolites (obviously, the zeolite structure factor plays a less important role in this case than in the case of isobutane formation).

Table 2 compares the hydrogen transfer activities of the parent HZSM-5, HY, and HM zeolites determined on the basis of the rates of propane and isobutane formation in the hydrogen transfer steps of the *n*-hexane cracking reaction. The data on the  $\alpha$ -activity (6) of these zeolites, which characterize the zeolite protolytic cracking activity (3), are also included in this table. The data presented demonstrate that the difference in the protolytic cracking activities of HM and Z-34 catalysts (2.08 and 1, respectively) is practically the same as the difference in the

TABLE 2

Alpha-Activity and Hydrogen Transfer Activity of Different Zeolites Determined on the Basis of Propane and Isobutane Formation Rates in the Hydrogen Transfer Steps of the *n*-Hexane Cracking Reaction

Type of activity	Relative activity <sup>a</sup>		
	Z-34	HY	HM
Alpha-activity	1	0.42	2.08
Hydrogen transfer activity (based on C <sub>3</sub> formation rate)	1	1.17	1.84
Hydrogen transfer activity (based on iC <sub>4</sub> formation rate)	1	6.15	10.5

<sup>a</sup> Activity of Z-34 catalyst has been taken as unity.

activities of these catalysts in hydrogen transfer (1.84 and 1, respectively) proceeding in the absence (or under weak influence) of the steric constraints. At the same time, <sup>27</sup>Al MAS NMR data show that the tetrahedral aluminium content is 2.1 times higher in the HM sample than in the Z-34 sample. All these data taken together strongly support the idea that (i) the active sites in HZSM-5 and mordenite (bridging OH groups associated with the framework aluminium atoms) display the same catalytic activity, and (ii) the difference in the "ideal" catalytic properties of HZSM-5 and mordenite (not distorted by the influence of the zeolite structure factor) is due to the difference in the number of these sites only. It should be noted that the situation can be different for mordenites with a higher aluminium content, when active sites cannot be considered as isolated sites. In this case the influence of acid site density on the catalytic activity (especially on hydrogen transfer activity) can be important (12–15).

According to the <sup>27</sup>Al MAS NMR data the tetrahedral aluminium content in the HY catalyst is 4.1 times higher than in the Z-34 catalyst. In spite of this, the "ideal" hydrogen transfer activity is practically the same for Z-34 and HY zeolites, and the protolytic cracking activity of HY zeolite is about 2.5 times lower than the corresponding activity of Z-34 zeolite (see Table 2). This means that (i) the catalytic sites (bridging OH groups) in HY zeolite display lower activity than the catalytic sites in HZSM-5, and (ii) the difference in the catalytic behaviour of these sites depends on the type of reaction catalyzed by them. Neither observation is unexpected, since it has been already shown that (i) the zeolite protolytic cracking activity, determined per framework aluminium atom, is higher with HZSM-5 in comparison with HY zeolites (12, 16), and (ii) the hydrogen transfer activity, in contrast with the protolytic cracking activity, is a function not only of the acid strength and number of the zeolite active sites, but also (and largely) of the density of these sites (12–15).

In our opinion, further work is needed to fully understand these features. Therefore, the detailed discussion of the catalytic properties of the active sites in HZSM-5 and HY zeolites, as well as in mordenites, will be presented in future publications.

### CONCLUSIONS

It is demonstrated that the experimental procedure of the recently proposed (4)  $\beta$ -test can be applied for quantitative estimation of propene, *n*-butene, and isobutene reactivities in the hydrogen transfer steps of *n*-hexane cracking reaction over zeolites of different pore structure. The results show that with large pore HY and HM zeolites, i.e., in the absence of steric constraints, isobutene is approximately 5 times more reactive in hydrogen transfer than *n*-butene. The latter, in turn, is about 1.3 times more reactive than propene. With medium pore HZSM-5, isobutene is only 1.2 times more reactive in hydrogen transfer than *n*-butene. The conclusion is drawn that this is due to the strong steric inhibition of formation of the transition state of the hydrogen transfer reaction between *n*-hexane and tert-butyl carbenium ion in HZSM-5 channels.

On the basis of the obtained results it is concluded that the  $\beta$ -test measures the "real" hydrogen transfer activity of zeolites, i.e., the activity that summarizes the effects of the acidic and structural properties of zeolites. An attempt is made to estimate the "ideal" zeolite hydrogen transfer activity, i.e., the activity determined by the zeolite acidic properties only. HM zeolite is found to be 1.8 and 1.6 times more active in the "ideal" hydrogen transfer than HZSM-5 and HY zeolites, respectively. These results, taken in consideration with the data on the zeolite tetrahedral aluminium content, strongly support the assumption that the bridging OH groups in HZSM-5 and mordenite display the same "ideal" catalytic activity (not distorted by the effect of the zeolite structure), and that this activity is higher than the observed "ideal" catalytic activity of the bridging OH groups in HY zeolite.

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