

SKELETAL ISOMERIZATION OF n-BUTANE OVER MORDENITE AND BETA ZEOLITES

Evzen BABUREK¹ and Jana NOVAKOVA²

*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
182 23 Prague 8, Czech Republic; e-mail: ¹baburek@jh-inst.cas.cz, ²povrch@jh-inst.cas.cz*

Received September 19, 1997

Accepted October 21, 1997

It was found that the addition of platinum (3 wt.%) substantially increases the total n-butane conversion and selectivity to isobutane over H-Beta zeolite. The same holds for H-Mordenite; however, the conversion significantly decreases in time at 350 °C due to the coking of the catalyst. The selectivity to isobutane is the highest at 300 °C over both zeolite types with platinum (over Pt/H-Beta 1.8 times higher than over Pt/H-Mordenite at almost the same conversion levels of 30 and 36%, respectively). The H-forms of both zeolite types are most selective at 250 °C, but the total conversion is low. The results obtained are related to the structural features of both zeolite types.

Key words: n-Butane isomerization; H-Mordenite; Pt/H-Mordenite; H-Beta; Pt/H-Beta.

The isomerization of n-butane to isobutane (IBA) makes n-butane more valuable because the former is used only as a component of fuels. The sources of n-butane are catalytic and steam crackers in petroleum refineries (7–12 and 2–5 wt.% of the C₄ fraction, respectively) as well as the wet natural gas¹. 2-Methylpropene, obtained by the dehydrogenation of IBA, is the starting compound for the synthesis of methyl *tert*-butyl ether (MTBE). MTBE becomes an important additive to gasoline as it enhances its octane number instead of undesirable aromatics and supplies the required oxygen. Bi-functional catalysts possessing both acidic and metallic sites have been employed for the isomerization of n-butane. The acid sites are assumed to govern the isomerization while the metallic sites catalyze the (de)hydrogenation processes^{1–9}. H-Forms of zeolites containing small amounts of noble metals replace the less environmentally friendly catalysts, which contained aluminium or organic chlorides on silica and alumina together with supported Ni or Pt (ref.¹).

Besides this important practical impact, the isomerization of n-butane is also very interesting reaction from the viewpoint of fundamental research. The concerted function of both types of active sites, spillover effects, acidity strength and number of acid sites, amount and dispersion of the metallic phase as well as the composition of the feed reactants have been investigated. The reaction pathways including hydrogenolysis, (de)hydrogenation, oligomerization, isomerization, cracking and hydride transfer have been assumed^{1–9}. The majority of authors agree on the bimolecular mechanism of the

reaction, in which *e.g.* the $C_4H_9^+$ ions, formed *via* protonation and dehydrogenation (or opposite steps) of n-butane, react with butene to yield protonated dimers ($C_8H_{17}^+$). These ions undergo further reactions from which the isomerization, cracking and hydride transfer lead to the formation of IBA (ref.⁹). Rigby *et al.*¹⁰ using *ab initio* quantum chemical calculations suggest intermediates of covalent alkoxide character rather than carbenium and carbonium ions or radical reactions.

The present contribution is focused on the comparison of two different structural types of acid zeolites of similar Si/Al ratio, H-Mordenite (HM) and H-Beta (H β), regarding their activity, selectivity and deactivation during the reaction of n-butane in the presence of hydrogen at various temperatures. Both pure H-forms of the catalysts as well as those with platinum are examined.

EXPERIMENTAL

Catalysts. NH_4^+ -forms of Mordenite ($SiO_2/Al_2O_3 = 20$) and Beta ($SiO_2/Al_2O_3 = 25$) zeolites, supplied by ConTek (U.S.A.), were employed as parent samples. They were deammoniated in the stream of hydrogen (see the treatment prior to catalytic tests) to H-forms, denoted later HM and H β . Pt/HM and Pt/H β (3 wt.% of Pt) were prepared by ion exchange with tetraammineplatinum(II) chloride (Aldrich Chem.) at room temperatures (for details see refs^{11,12}) and pretreated as the above parent samples. The ion exchange for platinum was rather high, 39 and 48% for HM and H β , respectively.

The samples were characterized by sorption capacities for Ar (prior to and after the catalytic runs). The values obtained prior to the catalytic experiments were measured after dehydration at 400 °C, the heating in vacuum at the same temperature was employed for the spent catalysts. A quartz spiral was used for these measurements; adsorption of Ar was measured at -195 °C under the pressure of 10 kPa. Surface areas of the parent samples were given by the supplier, as well as the weight losses after the heating to 800 °C (see Table I).

Ammonia released during the deammoniation of fresh samples without platinum (7 mg, heating rate 10 °C/min to 500 °C after dehydration carried out by 2 °C/min heating to 120 °C) was checked by a mass spectrometer (a Balzers QMG 420 quadrupole). After deammoniation, the samples were cooled to 120 °C and an excess of ammonia was adsorbed at this temperature. This excess was

TABLE I
Characteristics of catalysts

Catalyst Si/Al	Weight loss at 800 °C wt.%	Ar sorption capacity mmol/g ^a	v(OH) cm ⁻¹	NH ₃ desorbed mmol/g ^a	<i>T</i> _{max} of NH ₃ desorption °C	Surface area m ² /g
HM(11.1)	15	6.47	3 746, 3 671 vw ^b 3 609	1.3	334	500
Pt/HM	- ^c	6.13	3 746, 3 609	- ^c	- ^c	- ^c
	20	8.6	H β (13.9)	0.59	245	720
	- ^c	8.3	Pt/H β	- ^c	- ^c	- ^c

^a Undried sample; ^b very weak; ^c amount < 1 wt.%.

evacuated at the same temperature, and TPD (temperature programmed desorption) of ammonia was examined up to 500 °C with the same heating rate as during the preceding deammoniation. For comparison and as a reference sample, NH₄ZSM-5 with Si/Al = 25, supplied by Conteka, was also employed in the deammoniation and ammonia TPD measurements.

FTIR (Fourier transform infrared) spectra of OH groups were recorded after pretreatment at 500 °C in vacuum before the catalytic reactions using a Nicolet MX1E FTIR spectrometer with self-supported plates of zeolites (≈ 10 mg/cm²).

Catalytic tests were performed in a fixed-bed tubular quartz reactor with an inner diameter of 4 mm operated in continuous flow mode over 150 mg of the catalyst. The zeolites were heated in a hydrogen stream (60 ml/min) at the rate of 20 °C/min to 500 °C and held at this temperature for 3 h. The temperature was then decreased at the rate of 50 °C/min to the temperatures of catalytic runs (250, 300 or 350 °C).

n-Butane (Linde) mixed with hydrogen in 1 : 120 ratio was used as the feed reactant. The reactor effluent was collected using an automatic sampling valve system, stored in multiloop valves and subsequently analyzed with a Finigan 9001 gas chromatograph (30 m capillary column DB-1, supplied by J&W Scientific) equipped with a flame ionization detector.

RESULTS

Characteristics of Samples

Sorption capacities of fresh samples, weight loss during the heating, amounts of ammonia desorbed during TPD and the temperature maxima of NH₃ release together with frequencies of the vibration bands of OH groups are listed in Table I. Surface areas and weight losses are given only for the parent forms. The FTIR spectra of OH groups are displayed in Fig. 1. Ammonia released during the deammoniation of NH₄ forms of M

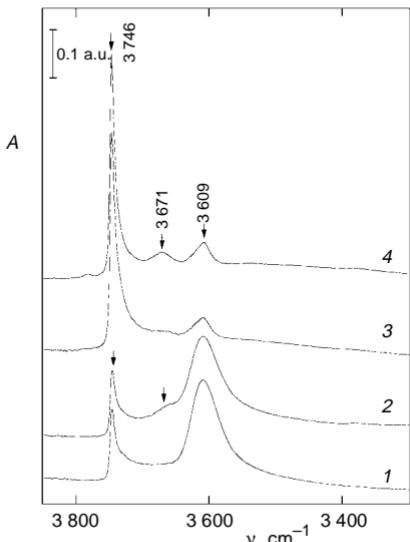


FIG. 1
FTIR spectra of OH groups of HM, Pt/HM, H β and Pt/H β catalysts. 1 Pt/HM, 2 HM, 3 Pt/H β , 4 H β

and β zeolites (and HZSM-5) as well as ammonia desorbed during the TPD from H-forms of the same zeolites are shown in Fig. 2.

Sorption capacities and surface areas are higher for the H β sample in line with its structural features (three mutually intercrossing 12-member ring channel system – two linear

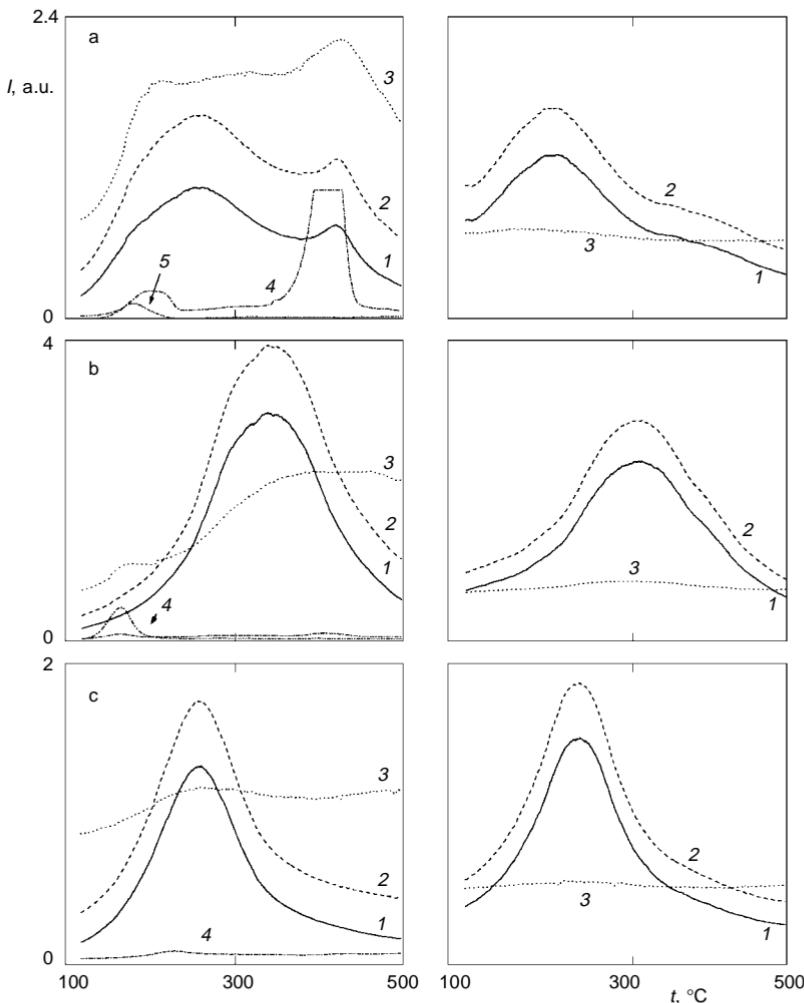


FIG. 2

Decomposition of ammonium forms and TPD of ammonia from H-forms of zeolites; left column: decomposition; right column: TPD of adsorbed ammonia. Ion intensities: 16^+ (1) and 17^+ (2) belong to ammonia, 18^+ (3) to water, 28^+ (4) predominantly to CO, 44^+ (5) to CO_2 . a H β , b HM, c HZSM-5

and one tortuous – with pore openings of the former channels approximately 5.7×7.5 Å and of the tortuous channel 5.6×6.5 Å (ref.¹³), while Mordenite contains one channel with 12 member ring openings (7.0×6.5 Å) and one intersecting channel with 8-member ring openings (5.7×2.6 Å).

The stretching vibrations of hydroxy groups are depicted in Fig. 1: H β zeolite contains a large fraction of SiOH groups (bands at 3746 cm^{-1}), which highly exceed in intensity the band of structural bridging OH groups (3609 cm^{-1}). The sample also exhibits a band at 3671 cm^{-1} , assigned to AlOH groups formed with extra-lattice Al. This latter band almost disappears in Pt/H β , probably because of the extraction of extra-lattice Al during the ion exchange. The SiOH band remains unchanged in Pt/H β , the intensity of the band of bridging hydroxyls slightly decreases. Pt/HM exhibits a very similar behaviour after the Pt exchange. However, the band of bridging hydroxyls of HM zeolite is more intensive compared to the band of SiOH groups and is much higher than that of bridging groups of the H β . The band assigned to extra-lattice Al is of much lower intensity. HM zeolite should have a higher amount of strong Brønsted acid sites than zeolite, which follows from their Si/Al ratio. The calculated factor approximately equals to 1.2 which, however, does not agree with the ratio of intensities of the structural OH bands (roughly 3 times higher for HM than for H β). Similarly, the number of strong Brønsted acid sites calculated from the ammonia desorption is by 2.1 times higher for HM than for H β . The number of strong acid sites in HM agrees with the theoretical value.

Both zeolites with platinum exhibit a very small decrease in intensities of the bands of bridging hydroxyls in spite of a relatively high extent of ion exchange. This can be explained by the known fact, that the decomposition of the tetraammineplatinum complex in vacuum (pretreatment for IR measurements was performed in vacuum) is accompanied by strong autoreduction^{12,14} of platinum(II). For that reason, protons generated from the decomposing ammonia ligands balance the zeolite charge instead of the previous $[\text{Pt}(\text{NH}_3)_4]^{2+}$, so that no substantial change in the number of bridging hydroxyls occurs. These hydroxyls must also be present after the pretreatment of the samples before the catalytic runs due to the replacement of Pt^{2+} by H^+ during the reduction in hydrogen.

The gases released during the deammoniation of both acid samples suggest a higher amount of impurities in the H β as can be seen in the left part of Fig. 2 – the evolution of CO (ion 28^+ , originating most probably from surface carbonates). It also can be seen in this figure that the dehydration before deammoniation was not quite complete, which follows from the increasing intensity of ion 18^+ (water) with increasing temperature; on the other hand, during the TPD of adsorbed ammonia (right part of the figure) the 18^+ intensity is constant and can be related to the background of the apparatus only.

Catalytic Activity

The total *n*-butane conversion is defined as the ratio X [%] = $[(a_0(\text{butane}) - a(\text{butane})) / a_0(\text{butane})] \cdot 100$, where a_0 and a are inlet and outlet amounts of butane (in mmol), respectively, and stand for the integrated gas chromatographic signals.

The dependences of the total conversion on time-on-stream over HM and Pt/HM are depicted in Fig. 3. Pt/HM exhibits the highest initial conversion at 350 °C, but becomes deactivated more rapidly than the other samples which, except of HM at 300 °C, retain their initial activity during the time interval measured. The same dependence is shown in Fig. 4 for H β and Pt/H β . All Beta samples retain their initial activity, a little lower than that over HM and Pt/HM, during the whole catalytic runs. The initial conversion over Pt/H β at 350 °C is stable during the time period measured, so that it is higher after 10 min than that over Pt/HM.

Selectivities to the individual products are defined as S [%] = $[a(\text{product}) / (a_0(\text{butane}) - a(\text{butane})) \cdot 100$. Table II lists the selectivities at the beginning of the reaction (after 10 min); the selectivities after 180 min are given in Table III. Isobutane (IBA) appears in all measurements performed, being predominantly accompanied by propane, whose frac-

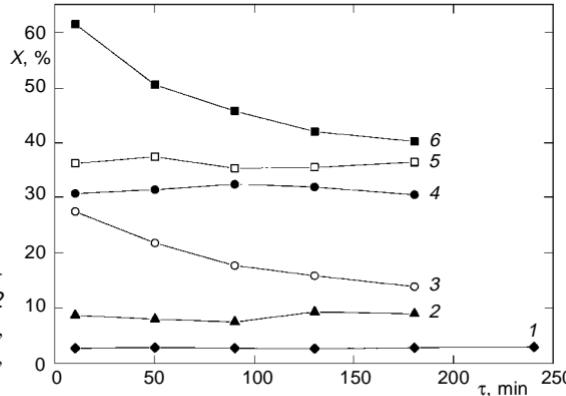


FIG. 3

Time dependence of conversion of *n*-butane over Mordenites. 1 250 °C, HM; 2 250 °C, Pt/HM; 3 300 °C, HM; 4 300 °C, Pt/HM; 5 350 °C, HM; 6 350 °C, Pt/HM

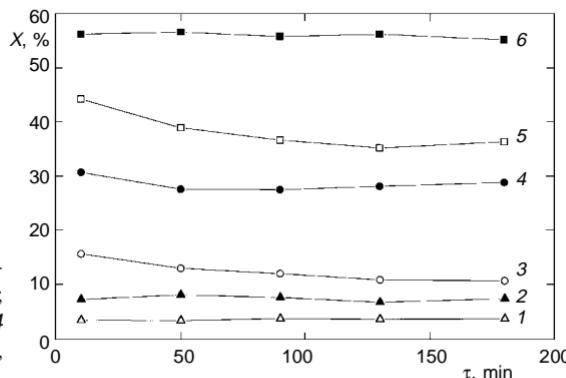


FIG. 4

Time dependence of conversion of *n*-butane over Beta catalysts. 1 H β , 250 °C; 2 Pt/H β , 250 °C; 3 H β , 300 °C; 4 Pt/H β , 300 °C; 5 H β , 350 °C; 6 Pt/H β , 350 °C

TABLE II

Selectivities (%) in n-butane reaction conversion over various catalysts and at different temperatures (°C) at the beginning of the reaction

Hydrocarbon	HM			Pt/HM			H β			Pt/H β		
	250	300	350	250	300	350	250	300	350	250	300	350
Methane	—	—	—	—	—	—	—	—	—	7.4	—	—
C ₂	—	30.3	42.3	—	7.7	24.6	—	—	—	28.8	—	6.9
Propane	28.1	32.1	22.3	46.0	36.2	20.2	40.2	21.1	40.2	—	8.8	23.3
Isobutane	57.0	28.4	30.0	50.1	49.2	16.9	46.2	28.0	16.0	55.5	74.8	37.4
Pentane	—	3.3	—	—	2.5	4.6	—	—	—	—	—	3.5
2-Methylbutane	—	6.0	3.2	—	4.3	4.6	—	—	—	—	—	—
2,2-Dimethyl-propane	—	—	—	—	—	—	—	—	4.2	37.9	4.1	2.1
2-Methylpentane	—	—	—	—	—	—	—	—	—	—	—	3.6
Aromatics	—	—	—	—	—	—	—	—	—	—	—	3.5

TABLE III

Selectivities (%) in n-butane conversion over various catalysts and at different temperatures (°C) after 180 min

Hydrocarbon	HM			Pt/HM			H β			Pt/H β		
	250	300	350	250	300	350	250	300	350	250	300	350
Methane	—	—	—	—	—	—	—	—	—	7.1	—	—
C ₂	—	30.5	41.7	—	10.5	13.0	—	—	—	25.4	—	3.6
Propane	28.9	33.9	22.8	53.5	34.9	32.6	34.5	21.8	35.8	—	5.9	24.6
Isobutane	55.3	26.8	30.1	43.2	45.1	33.1	52.2	27.7	16.1	64.8	80.6	37.0
Pentane	—	3.2	—	—	4.1	2.8	—	—	—	—	—	3.7
2-Methylbutane	—	5.6	3.0	—	5.5	2.8	—	—	—	—	—	—
2,2-Dimethyl-propane	—	—	—	—	—	—	—	—	5.8	32.8	5.8	2.4
2-Methylpentane	—	—	—	—	—	—	—	—	—	—	—	3.5
Aromatics	—	—	—	—	—	—	—	—	—	—	—	3.7

tion is substantially lower over Pt/H β . Methane in small amounts is formed only over H β and Pt/H β at the highest temperature of 350 °C. C₂ amounts are lower over both zeolite types with platinum, clearly at least at lower temperatures. C⁵⁺ hydrocarbons appear only in small concentrations, significant amounts are formed over Pt/H β at 250 °C. Aromatics in small amounts are also found over Pt/H β at 350 °C. It can be seen that the composition of products is not strongly affected by the time-on-stream, except Pt/HM. The selectivity to IBA is the highest over HM at the lowest temperature of 250 °C, with increasing temperature the selectivity to C₂ hydrocarbons predominates. The selectivity to IBA over Pt/HM does not change between 250 and 300 °C, but significantly decreases at higher temperatures. The changes in selectivities are not qualitatively different after short and longer time on stream except over Pt/HM at 350 °C; in the latter case the selectivity to IBA increases with time (cf. Tables II and III: 16.9 and 33.1% after 10 and 180 min, respectively). Propane behaves similarly to IBA over Pt/HM. The selectivity to C₂ hydrocarbons increases with increasing temperature for all the samples used.

Comparison of the total n-butane conversion with the yield of IBA (yield defined as $[a(\text{IBA})/a_0(\text{n-butane})] \cdot 100$) at 350 °C is shown in Table IV. The highest yield appears over Pt/H β (of about 20% at the conversion level of 56%). The lowest yield of IBA was measured over H β (of about 6% at the conversion level of 36%). An increasing yield of IBA (and decreasing conversion) with increasing time is found only for Pt/HM.

Sorption capacities measured after the reactions are plotted against the temperature of the catalytic runs in Fig. 5. Only a very small decrease with increasing temperature occurs over Beta zeolites and HM, whereas a substantial drop takes place over Pt/HM at 350 °C.

DISCUSSION

The conversion of n-butane to isobutane over *H-forms* of Beta and Mordenite zeolites with a similar Si/Al ratio does not exhibit very different behaviour regarding the total

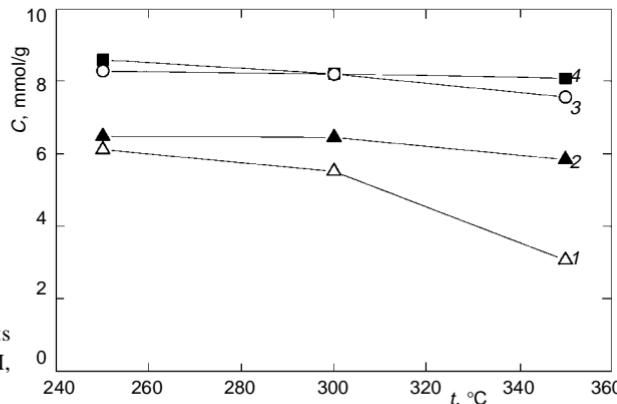


FIG. 5
Sorption capacities of catalysts after the reaction. 1 Pt/HM, 2 HM,
3 H β , 4 Pt/H β

conversion and selectivity to IBA formation. HM seem to be a little more selective, especially at the beginning of the reaction. The employment of molecular sieves with narrower pores would most probably have more pronounced effect, as follows from the studies by Richter *et al.*¹⁵ over SAPO-31 and SAPO-11. These catalysts were of low efficiency, which agrees with the assumption of bimolecular mechanism suppressed by insufficient space in the pores of SAPOs. Liu *et al.*¹⁶ also reported on low activity of n-butane isomerization over microporous catalysts. Krannilla *et al.*⁴ found highly predominating monomolecular mechanism of n-butane cracking over HZSM-5. The enhancing effect of decreasing reaction temperature is one of the features supporting the bimolecular mechanism of the isomerization, as was reported by Houzicka *et al.*⁸. Such an effect appears in our experiments (the highest selectivity to IBA at the lowest temperature of 250 °C) which can favour the assumption of the role of bimolecular mechanism; the di- and oligomerization reactions are enhanced by lower temperatures. However, the simultaneous formation of propane without significant appearance of pentanes suggests more complex reaction routes. The experimental conditions employed do not allow a more detailed insight into the reaction mechanism. At higher temperatures the side reactions (hydrogenolysis, cracking) participate at larger extent. The selectivity towards IBA strongly decreases especially over H β and C₂ hydrocarbons appear instead.

The introduction of platinum (due to the pretreatment located as larger particles partially at the surface of zeolite grains^{11,12}) results in higher conversion and selectivities to IBA (especially above 200 °C). Simultaneously, more evident differences among the *bifunctional Pt/H-forms* of the two zeolite structures appear: The total conversion is a little higher over PtHM, but the selectivity to IBA is higher over Pt/H β , almost twice at 300 °C. The temperature decrease in the IBA selectivity is shifted to higher temperature compared to pure H-forms. The increased reactivity of Pt/H-forms results in deactiva-

TABLE IV
Conversion (X, %) of n-butane and yields (Y, %) of isobutane over various catalysts at 350 °C

Reaction time min	HM		Pt/HM		H β		Pt/H β	
	X	Y	X	Y	X	Y	X	Y
10	30.8	9.3	61.5	10.4	44.3	7.1	56.3	21.0
50	31.5	9.3	50.5	12.1	39.0	6.5	56.6	20.5
90	32.5	9.2	45.8	13.2	36.7	6.3	55.8	20.6
130	32.0	9.5	42.1	13.4	35.2	6.1	56.2	20.4
180	30.6	9.2	40.3	13.3	36.3	5.8	55.1	20.4

tion of Pt/HM at 350 °C by coke deposits. In this case, the pore system of Mordenite is clearly less resistant to the pore plugging than the Pt/H β , which might be the main reason for more pronounced difference between these two zeolite structures. The decreased fraction of C₂ hydrocarbons compared to the H-forms (and also propane over Pt/H β) points to a decreased effect of side reactions, so that the (de)hydrogenation function of platinum favours the isomerization route.

The results obtained can be summarized as follows: The conversion of n-butane to isobutane does not substantially differ over HM and H β zeolites, the selectivity to IBA is a little higher over HM. These two zeolite types differ in the pore architecture and pore volume, as well as in the number and acid strength of hydroxyls. The selectivity to IBA is enhanced by lower reaction temperatures at which the total conversion is low, which supports the bimolecular reaction route. The incorporation of platinum enhances the activity as well as selectivity to IBA over both types of zeolites, suppresses the formation of side products and shifts the maximum selectivity to higher temperature compared to H-forms. The high activity at 350 °C results in deactivation of Pt/HM caused by coke deposits. The mono-dimensional linear channels of this zeolite are clearly easier plugged by coking than the channels of the Beta zeolite. Pt/H β was found to be the best catalyst for n-butane isomerization to IBA with highest selectivity (and no deactivation) obtained at 300 °C. The yield of IBA is comparable to or even higher than that reported in the literature. Experiments concerning the reaction mechanism are in progress.

The financial supports of the Grant Agency of the Czech Republic (Grant No. 203/96/0951) and Ministry of Education of the Czech Republic (OCD5.10/1997 in connection with the COST project No. D5/0002/94) are greatly appreciated.

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