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Journal of Catalysis 232 (2005) 366–377

JOURNAL OF CATALYSIS

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Isomerization of diisopropylnaphthalenes on wide-pore zeolites

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Received 25 October 2004; revised 24 February 2005; accepted 4 March 2005

Abstract

Experiments on the isomerization of diisopropylnaphthalenes (DIPNs) (i.e., of the slim isomer 2,6-DIPN and of the mixture of bulky isomers 1,3-DIPN and 1,7-DIPN) were carried out over wide-pore zeolites HY, H-beta, and H-mordenite and comparatively over an amorphous aluminosilicate. The external surface of the tested zeolites was very efficient in the isomerization of the DIPN isomers. However, the observed shape selectivity effects suggested that the activity of the pore entrances was more significant than the activity of the non-shape-selective external surface. In the products of isomerization of 2,6-DIPN over the H-beta and H-mordenite, the bulky 1,6-DIPN appeared more quickly than the slim 2,7-DIPN. However, a higher concentration of 2,7-DIPN in the product obtained over the HY zeolite indicated that the product was also formed inside the pores of this zeolite. The external surface of zeolites H-beta and HY revealed a higher activity in the isomerization of 1,7-DIPN than in the isomerization of 2,6-DIPN. Therefore, a better fit to the pore entrances of the former isomer than to the latter was proposed to explain this shape-selectivity effect. On the other hand, the H-mordenite catalyst was more active in the isomerization of 2,6-DIPN than in that of 1,7-DIPN. All tested zeolites demonstrated very low conversion of 1,3-DIPN when compared with the amorphous aluminosilicate.

Keywords: Diisopropylnaphthalene; Isomerization; Shape selectivity; Zeolite

1. Introduction

Reactions in which diisopropylnaphthalenes (DIPNs) are involved as products or substrates can deliver much important information about the structure and catalytic operation of zeolites. The critical sizes of DIPN isomers are comparable to the dimensions of the channels of wide-pore zeolites. Therefore, high β,β-selectivity (i.e., high yield of 2,6-DIPN and 2,7-DIPN) is expected in the product obtained over zeolites such as mordenite, faujasite, beta, and ZSM-12. Depending on assumed bond lengths and the method of calculation, the dimensions of the individual DIPN isomers are sometimes different [1–5]. However, the following order of increasing critical size of DIPN molecules can be arranged:

$$\begin{aligned}&\text{2,6-DIPN} \leqslant \text{2,7-DIPN} < \text{1,6-DIPN} \leqslant \text{1,5-DIPN}\\ &\quad \ll \text{1,7-DIPN} < \text{2,3-DIPN} < \text{1,4-DIPN} < \text{1,3-DIPN}.\end{aligned}$$

Of these isomers, only 2,6- and 2,7-DIPN can easily fit into the empty spaces inside the pores of wide-pore zeolites. The formation, reaction, or diffusion of other DIPN isomers inside the pores of the wide-pore zeolites seems rather impossible.

An evidently higher selectivity for 2,6-DIPN than for 2,7-DIPN in isopropylation of naphthalene carried out over mordenite catalysts is another example of the shape selectivity [1,2,6–14]. The origin of such a high 2,6-DIPN/2,7-DIPN ratio is still widely discussed in the literature [1–9,15].

Dealumination of mordenite and deposition of inactive species (e.g., cerium) on the external surface were reported to be very effective methods for increasing the 2,6-DIPN/2,7-DIPN ratio and the β-selectivity in the alkylation product [2,6,7,9–13].

Independently of the selectivity of the zeolite catalyst, bulky DIPN isomers were always present in the alkylation product together with the slim 2,6-DIPN and 2,7-DIPN. It is frequently suggested that shape-selectivity effects are di-

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doi:10.1016/j.jcat.2005.03.009

minished by non-shape-selective catalysis on the external surface. However, not all observations can be explained by non-shape-selective reactions occurring on the external surface of the zeolite. For instance, the unusually high concentration of bulky isomers, such as 1,4-DIPN and 1,3-DIPN, can sometimes be observed in the product of alkylation of naphthalene with propylene over wide-pore zeolites [16]. Therefore, a shape-selectivity effect of pore entrances was proposed to explain the high concentration of DIPN isomers with both substituents attached to the same naphthalene ring.

Examples of shape-selectivity effects correlated with the external surface of zeolites and pore entrances were suggested earlier. Fraenkel et al. [17] and Derouane et al. [18] proposed that "nests" present on the external surface of HZSM-5 zeolite crystals can play an important role in the selective formation of 2,6- and 2,7-dimethylnaphthalene. Furthermore, Martens et al. [19] proposed "pore mouth" catalysis to explain the shape-selectivity effects observed in the isomerization of long-chain paraffins over ZSM-22 zeolite.

To assess the external surface influence on the composition of the DIPN product, Schmitz and Song [2,20] tested the isomerization of 2,6-DIPN (with simultaneous alkylation by propylene) over mordenite catalysts with various silica-to-alumina ratios. Regardless of the experimental conditions, DIPN isomers other than 2,7-DIPN and triisopropylnaphthalenes were quite abundant in the product. To explain these results, the involvement of pore entrances of zeolite in catalytic reactions was proposed [16].

In this study, experiments on the isomerization of 2,6-DIPN and a mixture of 1,3-DIPN and 1,7-DIPN were performed over wide-pore zeolites: HY, H-mordenite, and H-beta. The experiments can provide valuable information on reactions occurring on the zeolites and localize them on or in zeolite crystals, because 2,6-DIPN can be transformed both inside the zeolite pores and on the external surface, whereas 1,3-DIPN and 1,7-DIPN can react only on the external surface. For comparison, both isomerization tests were also carried out over an amorphous aluminosilicate. This work is a continuation of previous investigations on DIPN shape selectivity in the alkylation of naphthalene [16] and the disproportionation of isopropylnaphthalene (IPN) [15] performed over wide-pore zeolites.

2. Experimental

2,6-DIPN (99.9% pure, GC and GC/MS analysis, melting point 68.5 °C) was isolated from DIPN mixtures by distillation and crystallization. The main impurity was 2,7-DIPN. A solution of 2,6-DIPN (20 mol%) in decalin was used as a feed in the first set of isomerization experiments. In the second set of experiments, a mixture of 1,3-DIPN and 1,7-DIPN, without any solvent, was used. The mixture had been isolated by careful distillation of the DIPN fraction and contained 93.8 mol% DIPN isomers, 1.0% IPN, and 0.5% TIPN, and the remainder consisted mainly of alkylnaphthalenes C_{14}–C_{17} with substituents other than isopropyl (molecular masses by GC/MS, 184, 198, and 226). The isomeric composition of DIPN was as follows: 64.6% 1,3-DIPN, 32.8% 1,7-DIPN, and 2.6% 2,3-DIPN.

Table 1
Properties of the tested catalysts

Catalyst	SiO_2/Al_2O_3 ratio	External surface area (m^2/g)	Pore volume (cm^3/g) Total	Pore volume (cm^3/g) Micropores	NH_3 TPD (mmol/g)
HY[a]	5.8	59	0.33	0.25	2.18
HB	25	230	0.67	0.13	1.88
HM	84	83	0.34	0.19	2.08
ASA	13.4	395[b]	0.64	–	1.39

[a] Na_2O content 3.5%.
[b] Total surface area.

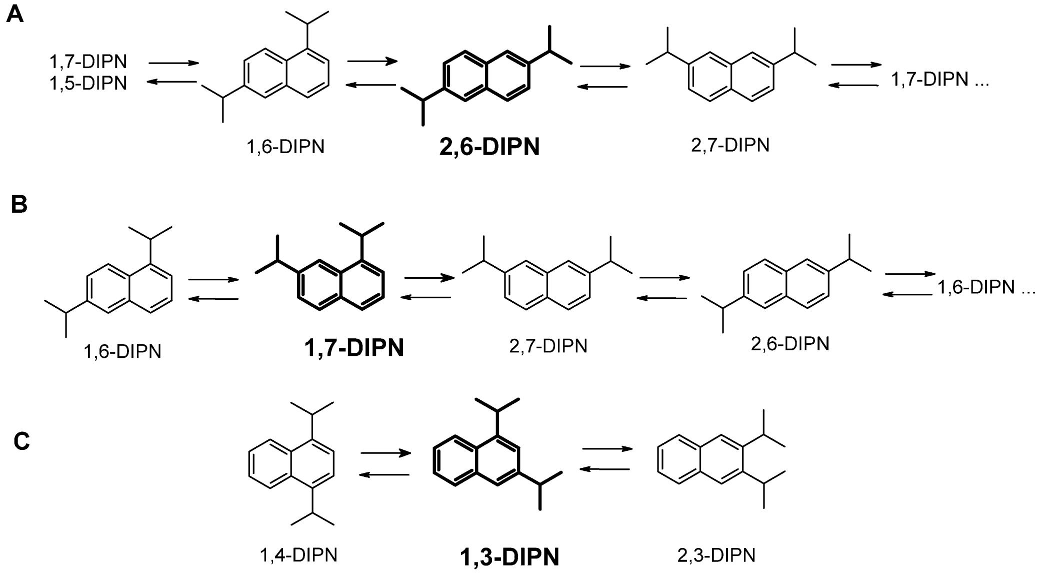
Three zeolite catalysts, HNaY (HY), H-beta (HB), and H-mordenite (HM), and amorphous aluminosilicate (ASA) were tested in both reactions. Characteristics of the catalysts are listed in Table 1. The porosity of samples was determined with an automatic Micrometrics Gemini II apparatus. Comparative tests of acidity (NH_3 TPD in the range of 100–600 °C) were performed with a GC apparatus with a thermal conductivity detector.

Before each experiment, the catalysts were activated at 450 °C in a flow of air for at least 2 h. Subsequently the air stream was replaced with nitrogen, and the temperature was lowered to the experimental temperature of 250 °C. We carried out isomerization experiments in a fixed-bed reactor (5 g of catalyst) by recirculating the mixture of reagents through the catalyst bed at $F/W = 70\ g/(g_{cat}\ h)$. Such a flow made it possible to pass the reactants through the catalyst bed every 6 min. Samples of products were analyzed by GC equipped with FID, with the use of a 60-m-long HP-Innowax capillary column [21]. Gaseous hydrocarbons, if present, were dissolved in the liquid products.

The concentration of a given DIPN isomer was calculated in relation to the total content of DIPN isomers. To observe transformations of a starting DIPN isomer in isomerization, the isomerization conversion was defined as the difference between the concentrations of the isomer (in relation to all DIPN isomers) in the feed and actual, divided by its concentration in the feed and multiplied by 100%. The isomerization conversion calculated in such a way indicated only the alteration in isomeric composition by both intramolecular and intermolecular isomerization, but ruled out the loss of the DIPN isomer (or isomers formed from it) in other reactions, such as disproportionation and dealkylation.

3. Results

Possible reactions of intramolecular isomerization of the tested DIPNs are shown in Scheme 1. 2,6-DIPN (Scheme 1A) can directly isomerize to 1,6-DIPN and 2,7-DIPN, which can further react to 1,5-DIPN and 1,7-DIPN. 2,6-



Scheme 1. Scheme of the intramolecular isomerization of 2,6-DIPN (A), 1,7-DIPN (B), and 1,3-DIPN (C).

DIPN and 2,7-DIPN are thermodynamically the most preferred isomers [4,6,22]. About 40% of each isomer is present in the thermodynamic equilibrium mixture at 250 °C. Other isomers are less abundant in the mixture: α,β-isomers (i.e., 1,3-DIPN, 1,6-DIPN, and 1,7-DIPN) in the range of 4–8%, 2,3-DIPN at $< 1\%$, and only traces of α,α-isomers. 1,3-DIPN, 1,4-DIPN, and 2,3-DIPN can be formed from 2,6-DIPN only via intermolecular reactions [7]. Conversion of 1,7-DIPN to 2,7-DIPN is the major isomerization reaction (Scheme 1B) and is thermodynamically preferred. Direct isomerization to 1,6-DIPN is also possible, although it is less favored. Secondary isomerizations of 1,6-DIPN and 2,7-DIPN lead to 2,6-DIPN. 1,3-DIPN can directly isomerize to 1,4-DIPN and 2,3-DIPN (Scheme 1C). Among these isomers 1,3-DIPN is the most preferred thermodynamically [4,22]. Other DIPN isomers can be formed only by intermolecular reactions.

3.1. Isomerization of 2,6-DIPN

The time dependencies of the product composition, obtained during 2,6-DIPN isomerization carried out over various catalysts, are shown in Fig. 1. The DIPN, IPN, and TIPN content in the recycled product made it possible to assess the basic reactions of DIPN other than isomerization, such as transalkylation, disproportionation, and dealkylation. The content of IPN and TIPN in the reaction mixture increased with recirculation time at the expense of DIPN for all tested catalysts, but the amorphous aluminosilicate (Fig. 1A) revealed the highest activity. After 6 h, the total content of DIPN in the recirculated mixture dropped to 52% over the ASA catalyst and to 70–88% over the zeolites. This corresponds to 76% conversion of DIPN to IPN, TIPN, and other products on the ASA, ca. 40% conversion on the HY and HB zeolites, and 21% conversion on the HM catalyst.

Initially, disproportionation of DIPN to IPN and TIPN was the main reaction (apart from isomerization) over the ASA catalyst. However, the slightly higher content of IPN than TIPN (Fig. 1A) indicates dealkylation of DIPN. At longer recirculation time the dealkylation products were formed more intensively than disproportionation products, and after 6 h the IPN content in the product was evidently higher than that of TIPN. The content of by-products other than IPN and TIPN also increased with recirculation time. Thus, the initial selectivity of the reaction of DIPN to IPN and TIPN decreased from 96 to 86% after 6 h. The longer the reaction time, the greater was the amount of naphthalene and alkylnaphthalenes with alkyl substituents other than isopropyl in the product. Other by-products, such as alkyltetralines and nonaromatic hydrocarbons, were also detected.

As indicated by the higher content of IPN than TIPN, the zeolite catalysts revealed activity in both disproportionation and dealkylation. By-products were also more abundant over the zeolite catalysts than over the ASA. A relatively low difference between IPN and TIPN content on the HM zeolite (Fig. 1D) resulted from low overall activity of the catalyst in the tested reactions.

The time dependencies of the DIPN isomeric composition in experiments of isomerization of 2,6-DIPN carried out over various catalysts are shown in Fig. 2.

The ASA catalyst was more efficient in 2,6-DIPN isomerization than were the zeolites. An isomerization conversion higher than 60% was achieved over the ASA catalyst after 2 h, whereas over the HY, HB, and HM catalysts, conversions of 43, 31, and 18% were achieved, respectively, after 6 h of recirculation of the DIPN mixture.

The isomeric DIPN composition indicates that the intramolecular isomerization of 2,6-DIPN (according to Scheme 1A) was more intensive than the intermolecular reaction for all tested catalysts. The concentrations of 1,6- and 2,7-

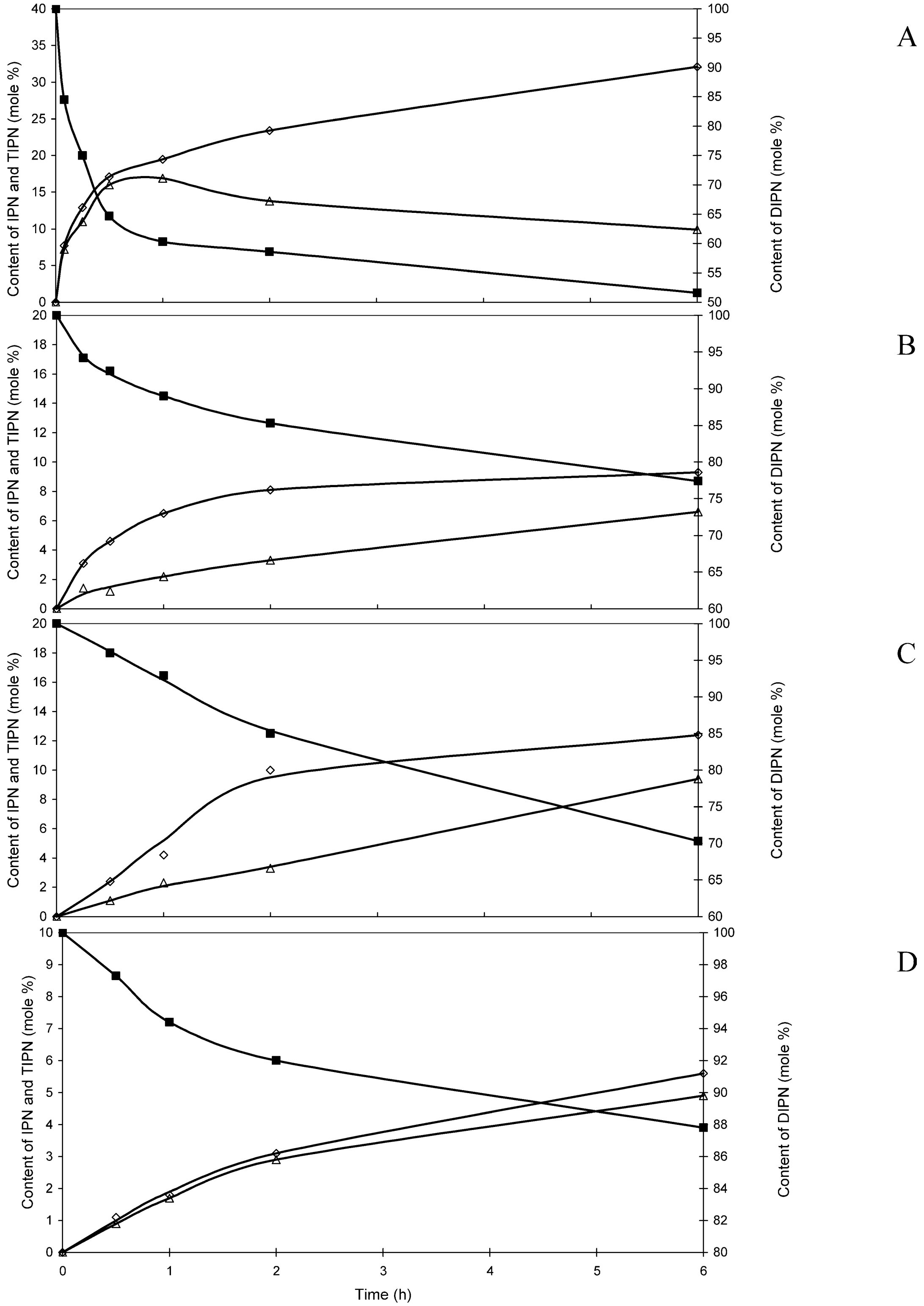


Fig. 1. Product composition as a function of the 2,6-DIPN isomerization time for different catalysts: ASA (A), HY (B), HB (C), and HM (D). Symbols: ■, DIPN; ◇, IPN; △, TIPN.

DIPN increased more quickly than those of 1,3- and 2,3-DIPN (Fig. 2).

Over the ASA catalyst the content of 1,6-isomer initially increased more quickly than that of the 2,7-isomer (Fig. 2A). However, after approaching 10–11%, the content of 1,6-DIPN dropped slightly, whereas that of 2,7-DIPN still increased. This was due to the higher equilibrium concentration of 2,7-DIPN than 1,6-DIPN. A faster increase in the

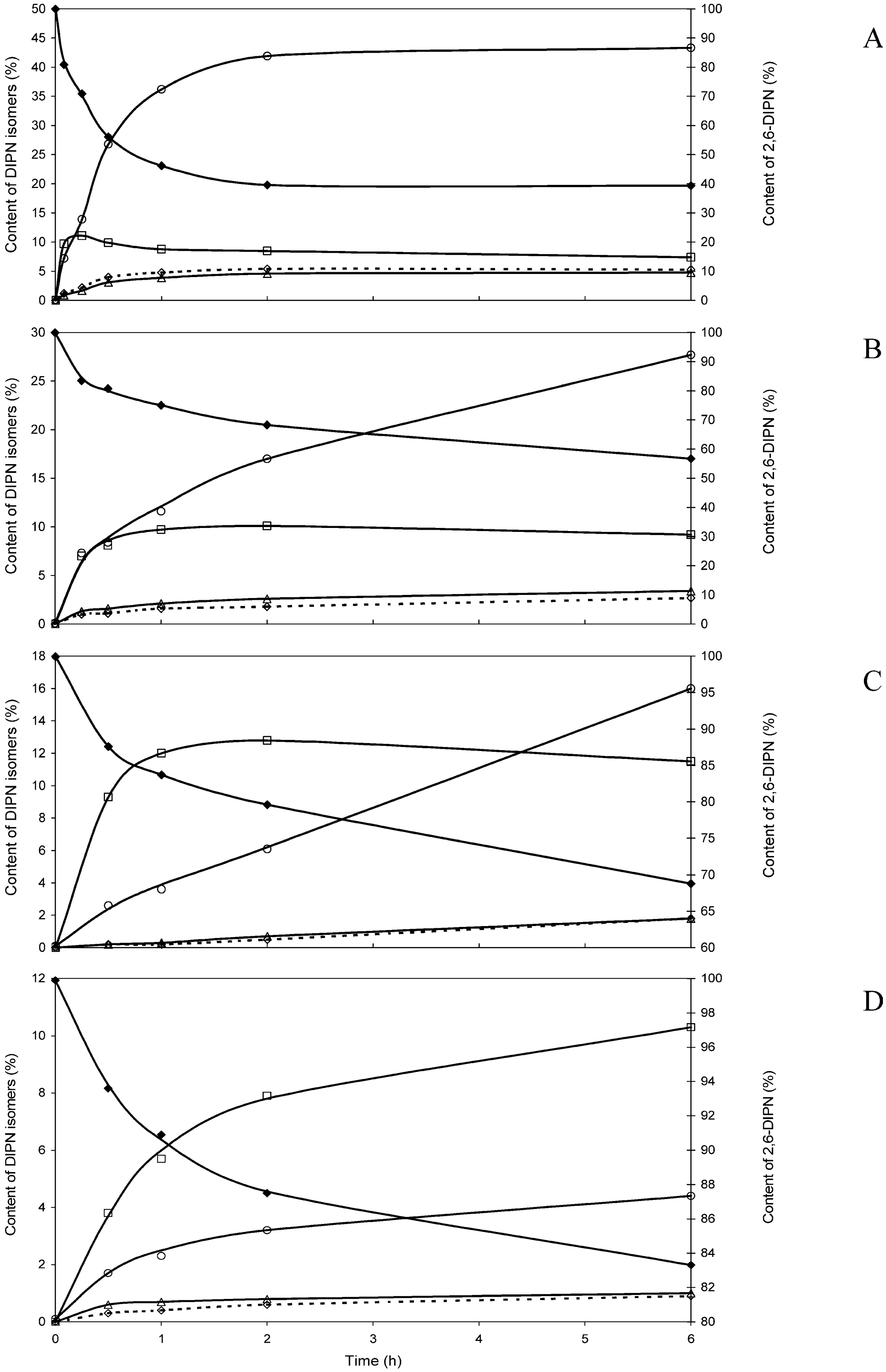


Fig. 2. Composition of DIPN isomers in the isomerization of 2,6-DIPN over different catalysts: ASA (A), HY (B), HB (C), and HM (D). Symbols: ◆, 2,6-DIPN; □ 1,6-DIPN; ○, 2,7-DIPN; △, 1,7-DIPN; ◇, 1,3-DIPN + 2,3-DIPN (dashed line).

1,6-DIPN content than in that of 2,7-DIPN was more evident for the HB and HM catalysts (Figs. 2C and 2D), where the content of the former isomer was several times higher than that of the latter. On the other hand, for the HY zeolite the content of 2,7-DIPN was slightly higher than that of 1,6-DIPN, even for low 2,6-DIPN isomerization conversion (Fig. 2B). A comparison of isomerization selectivities for similar conversion levels, as shown in Table 2, confirms this

Table 2
Comparison of catalysts in reactions of 2,6-DIPN for similar DIPN conversion level

Catalyst	DIPN conversion (%)	Selectivity (%)		Conversion of 2,6-DIPN in isomerization (%)	Selectivity of isomerization		
		Disproportionation	Dealkylation		1,6-DIPN	2,7-DIPN	Intermolecular
ASA	15	93	3	19	51.1	37.9	6.3
HY	14	45	32	32	32.0	53.8	5.7
HB	15	44	45	20	63.1	30.0	2.5
HM	12	80	6	17	62.0	26.5	5.4

observation. The selectivity of isomerization to 2,7-DIPN was higher than that to 1,6-DIPN only on the HY zeolite, whereas on the ASA catalyst and, especially, on the HB and HM zeolites, a significantly higher 1,6-DIPN selectivity was observed.

3.2. Isomerization of the 1,3-DIPN and 1,7-DIPN mixture

The results of isomerization of the 1,3-DIPN and 1,7-DIPN mixture are shown in Figs. 3 and 4. Similar to the isomerization of 2,6-DIPN, the ASA catalyst revealed the highest activity in the disproportionation and dealkylation of the DIPNs (Fig. 3). After 6 h, the content of DIPN decreased by 44%, whereas over the HB, HY, and HM zeolites it dropped by only 15, 10, and 5%, respectively.

The simultaneous increase in the IPN and TIPN contents indicates that disproportionation was the main side reaction of the DIPNs over the ASA catalyst, but the prevalence of IPN over TIPN shows that dealkylation of DIPN also occurred. All tested zeolites were more active in dealkylation than in disproportionation and yielded significantly larger amounts of IPN than TIPN. Other by-products were also quite abundant in the product.

In Table 3 selectivities and isomerization conversions, obtained for various catalysts in isomerization of the 1,3-DIPN and 1,7-DIPN mixture, are compared. In the case of the ASA catalyst, the disproportionation selectivity was slightly higher than the dealkylation selectivity, whereas over the zeolites dealkylation was the main side reaction. It is necessary to mention here that the sum of selectivities calculated for the ASA catalyst is greater than 100% because of high conversion of feed impurities in relation to the conversion of DIPN at early stages. Moreover, the negative isomerization conversion of 1,3-DIPN calculated for the ASA catalyst can be explained by a higher disproportionation or dealkylation reactivity of 1,7-DIPN (or DIPN isomers formed from 1,7-DIPN) than 1,3-DIPN. The loss of 1,7-DIPN was then slightly greater than that of 1,3-DIPN, so the content of 1,3-DIPN in the DIPN isomeric mixture had apparently increased.

The intramolecular isomerization to 1,4-DIPN was not a significant reaction of 1,3-DIPN (Scheme 1C), for thermodynamical reasons [4,6,22]. The content of 1,4-DIPN in the products was always lower than 1.4%. Any visible changes in the 1,3-DIPN content were mainly due to the intermolecular reactions. Therefore, the total content of 1,3-DIPN, 1,4-DIPN, and 2,3-DIPN is plotted in Fig. 4, instead of the 1,3-DIPN content. In Fig. 4D, however, the plot is omitted because of very small changes in the isomeric distribution due to the low activity of the HM catalyst in the tested reactions.

The loss of 1,7-DIPN was faster than that of 1,3-DIPN, 1,4-DIPN, and 2,3-DIPN. This is especially evident for the zeolite catalysts, where the total content of 1,3-DIPN, 1,4-DIPN, and 2,3-DIPN changed very slightly. After 6 h it dropped from 67.2% in the feed down to 64.0, 65.7, and 66.4% over the HB, HY, and HM zeolites, respectively, and down to 20% over the ASA catalyst. This means that more than 70% of 1,3-DIPN isomerized over the ASA (both according to the intramolecular and intermolecular mechanisms), whereas over the HB, HY, and HM zeolites only 7.6, 1.9, and 1.7% isomerized, respectively. The lower activity of zeolites can be attributed to the limited access of the 1,3-isomer to the active zeolite centers.

The isomerization of 1,7-DIPN occurred very intensively on the tested catalysts, except for the HM zeolite (Fig. 4). A quite high isomerization conversion of 1,7-DIPN was obtained over the HB and HY zeolites (87 and 59%, respectively, after 6 h of recirculation time) when compared with that achieved over the ASA catalyst (83%). Similarly, higher conversion of 1,7-DIPN over the HY and HB zeolites than over the ASA can be observed at the same DIPN conversion level (Table 3). On the other hand, only 4% of 1,7-DIPN isomerized over the HM zeolite, even after 6 h.

From the time dependencies of the isomeric composition of DIPN, obtained for the isomerizations carried out over all tested catalysts (Fig. 4 and Table 3), it is evident that 1,7-DIPN isomerized mainly to 2,7-DIPN and consecutively to 2,6-DIPN and further to 1,6-DIPN. Nevertheless, direct isomerization of 1,7-DIPN to 1,6-DIPN is also probable. An insignificant influence of intermolecular reactions on the isomeric composition of DIPN cannot be ruled out.

4. Discussion

4.1. Mechanism of DIPN isomerization

As can be seen from Figs. 2 and 4, intramolecular isomerization of DIPNs occurred more efficiently than intermolecular isomerization, for all tested catalysts under given conditions. In 2,6-DIPN isomerization (Fig. 2), 1,3- and 2,3-DIPN, which can arise from 2,6-DIPN only by intermole-

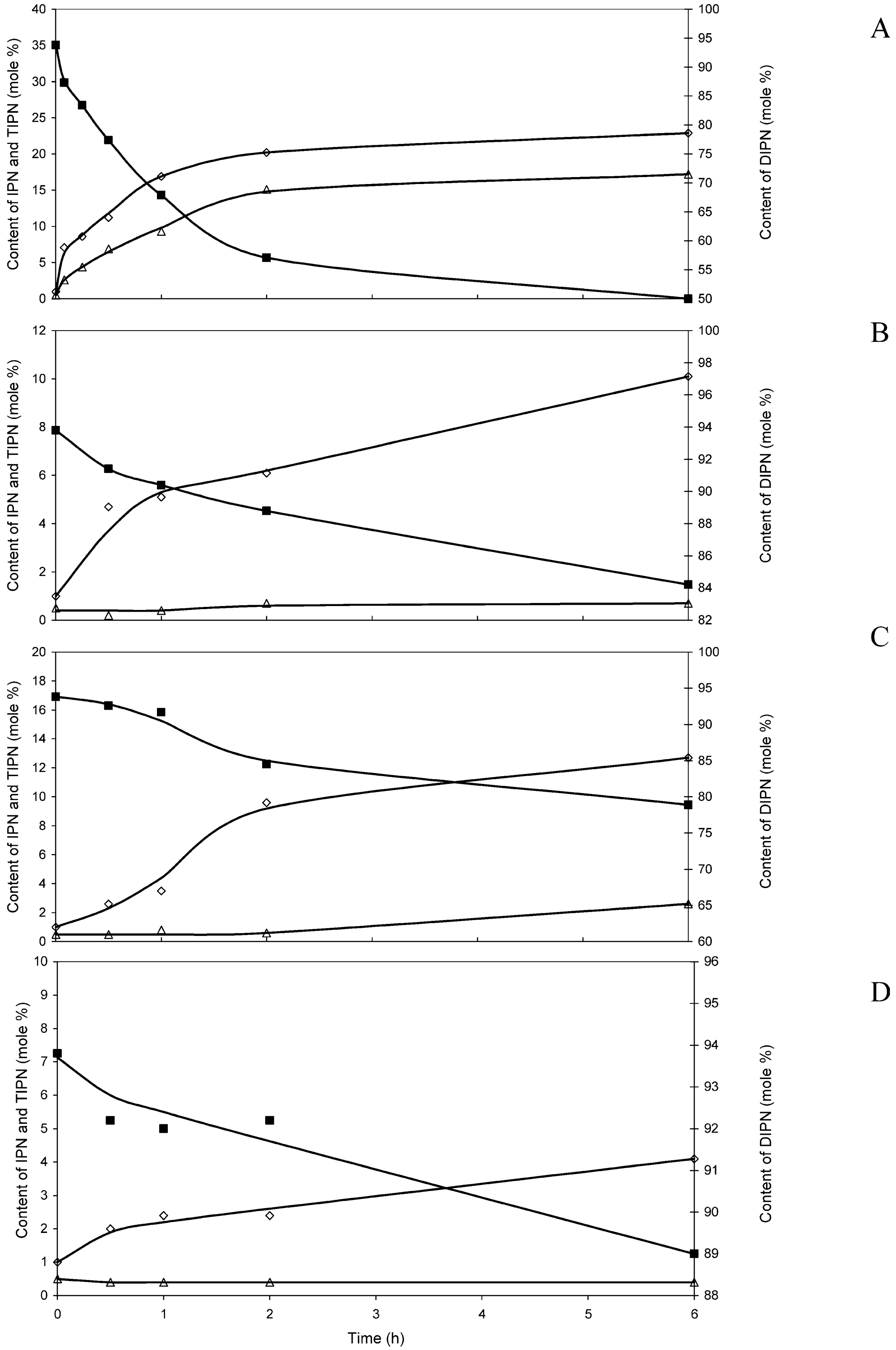


Fig. 3. Time dependencies of the product composition in the isomerization of the 1,3-DIPN and 1,7-DIPN mixture obtained for different catalysts: ASA (A), HY (B), HB (C), and HM (D). Symbols as in Fig. 1.

cular isomerization, were formed relatively slowly as compared with the other isomers. Initially (0.08 h), the isomeric mixture of DIPN obtained over the ASA catalyst contained only 1.2% of the 1,3-DIPN and 2,3-DIPN isomers, whereas the other isomers constituted 18.1%. After 6 h these groups of isomers amounted to 5 and 56%, respectively. This means that more than 90% of DIPN isomers were formed by intramolecular isomerization.

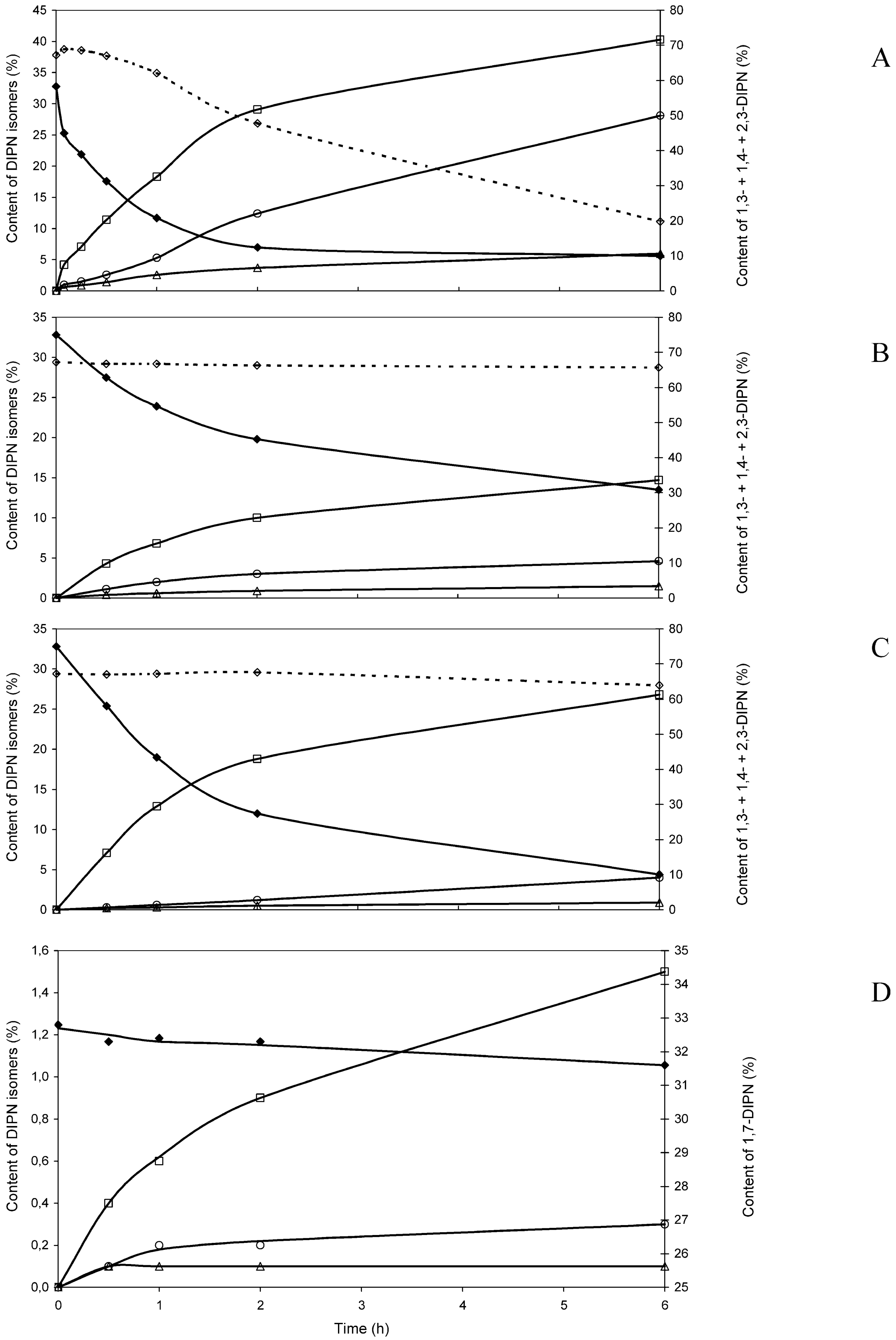


Fig. 4. Composition of DIPN isomers in the isomerization of the 1,3-DIPN and 1,7-DIPN mixture over different catalysts: ASA (A), HY (B), HB (C), and HM (D). Symbols: ◇, 1,3-DIPN + 1,4-DIPN + 2,3-DIPN (dashed line); ◆, 1,7-DIPN; □, 2,7-DIPN; ○, 2,6-DIPN; △, 1,6-DIPN. Remark: In Fig. 4D a content of 1,3-DIPN + 1,4-DIPN + 2,3-DIPN is omitted.

Table 3
Comparison of catalysts in reactions of 1,3-DIPN and 1,7-DIPN for similar DIPN conversion level

Catalyst	DIPN conversion (%)	Selectivity (%)		Isomerization conversion		Isomerization selectivity		
		Disproportionation	Dealkylation	1,3-DIPN	1,7-DIPN	2,7-DIPN	2,6-DIPN	1,6-DIPN
ASA	7	65 (55)[a]	54 (45)[a]	−2	23	66.7	15.9	9.5
HY	5	8	88	1	40	69.9	21.0	6.3
HB	10	3	91	2	63	87.4	5.6	2.3
HM	5	0	93	2	4	68.2	13.6	4.5

[a] Due to high conversion of feed impurities in relation to conversion of DIPN the sum of selectivities is > 100%. Therefore, in parentheses relative disproportionation and dealkylation selectivities are calculated.

Zeolites were less effective catalysts in the intermolecular isomerization of 2,6-DIPN than the ASA, and still lower yields of 1,3-DIPN and 2,3-DIPN were achieved (Fig. 2). This appears reasonable if we assume that, because of steric hindrance inside the pores, only the external surface of the zeolite crystals participates in intermolecular isomerization, leading to these bulky DIPN isomers. From Table 1 it is evident that the external surface area of the zeolites is smaller than the total surface area of the ASA catalyst.

More intensive intramolecular than intermolecular isomerization is observed in the isomerization experiments with the 1,3-DIPN and 1,7-DIPN mixture (Fig. 4). The isomerization conversion of 1,7-DIPN was always significantly higher than that of 1,3-DIPN because the favored intramolecular isomerization of 1,7-DIPN to 2,7-DIPN was possible (Scheme 1B), whereas isomerization of 1,3-DIPN to the thermodynamically less stable 1,4-DIPN (Scheme 1C) was observed to a small extent only at early stages. Quite intensive intermolecular isomerization was noticeable only on the ASA catalyst after a recirculation time longer than 0.5 h (Fig. 4A). From the above considerations it is obvious that in both sets of isomerization experiments, carried out over zeolite catalysts, the influence of the intermolecular isomerization on the isomeric composition of DIPNs was less significant than that of the intramolecular isomerization.

Examination of the isomeric composition of the DIPN mixtures obtained on the ASA catalyst led to conclusions about the mechanism of isomerization of the DIPN isomers under conditions not influenced by steric hindrances. First, the suggestion by Tasi et al. [4], that 2,6-DIPN and 2,7-DIPN are able to transform into each other via a 1,2-isopropyl shift, seems to be right. Both isomerization of 2,6-DIPN to 2,7-DIPN (Fig. 2A) and consecutive isomerization of 2,7-DIPN to 2,6-DIPN, in the experiment with isomerization of 1,7-DIPN (Fig. 4A), are evident.

Second, the 1,2-isopropyl shift between the α- and β-positions (in both directions) occurred faster than that between two β-positions. In the 2,6-DIPN isomerization test (Fig. 2A), the concentration of 1,6-DIPN very quickly approached 10–11%, a value close to that predicted by thermodynamics [4,6,22], whereas the concentration of 2,7-DIPN increased more slowly but to higher values. Similarly, isomerization of 1,7- to 2,7-DIPN (Fig. 4A) seemed to proceed more quickly than the consecutive isomerization of 2,7- to 2,6-DIPN, and the concentration of the 2,7-isomer in the recirculated mixture was several times higher than that of the 2,6-isomer.

4.2. *Role of the pore entrances in the isomerization of 2,6-DIPN*

If we assume that the recirculated mixture of reagents consists of partial products formed at different places in the zeolite crystals, we can expect, during isomerization of 2,6-DIPN, that 2,7-DIPN constitutes 100% of the isomerization product formed inside the zeolite pores. A partial product formed on the non-shape-selective external surface is predicted by kinetics and thermodynamics and is expected to be similar to that obtained on the ASA. This means that it should contain more 1,6- than 2,7-DIPN if the isomerization conversion of 2,6-DIPN is lower than 20%, but 2,7-DIPN can be expected to be prevalent for a higher conversion. In addition, the concentration of other isomers should then increase, mainly that of 1,7-DIPN and 1,3-DIPN, because for longer reaction times the composition of the isomeric mixture formed on the non-shape-selective surface approaches thermodynamic equilibrium. We can also suppose that almost all intermolecular reactions occur on the external surface because of steric hindrances of bulky products. Even a possible intermolecular isomerization of 2,6- to 2,7-DIPN in the narrow zeolite pores may be much suppressed, because of the direct neighborhood of two isopropyl substituents from two neighboring 2,6-DIPN molecules (cf. Fig. 8 and the discussion in [15]).

The results of 2,6-DIPN isomerization show that the contribution of the external surface to the product composition was very important for all zeolites. In particular, the isomeric mixtures of DIPN achieved over the HM and HB catalysts were enriched in the bulky 1,6-DIPN (Figs. 2C and 2D and Table 2). Over the HB zeolite the 2,7-DIPN content surpassed that of 1,6-DIPN only for long recirculation times because it approached thermodynamic equilibrium. In the DIPN mixture recirculated over the HY zeolite (Fig. 2B), a higher content of 2,7-DIPN than 1,6-DIPN can be observed even initially. In this case we can deduce that part of the product was derived from the pores of the zeolite. One should note that the windows of zeolite HY (0.74 nm) are slightly wider than the pores of zeolites beta (0.72 × 0.62 and 0.55 × 0.5 nm) and mordenite (0.70 × 0.67 nm).

The higher concentration of 1,6-DIPN than 2,7-DIPN obtained over the HM and HB zeolites at early stages (isomerization conversion $< 20\%$, Figs. 2C and 2D and Table 2) is compatible with results achieved over ASA and follows the kinetics of isomerization of 2,6-DIPN. If we consider the high concentration of bulky 1,6-DIPN in the product obtained over wide-pore zeolites at low conversion level, with respect to the size of molecules and zeolite pores, we can conclude that a significant part or even the majority of the reactions occurred on the external surface of the zeolites, that is, on the "true" external surface (i.e., non-shape-selective) or in the pore entrances but not inside the pores.

From the results of 2,6-DIPN isomerization it is difficult to decide whether the reaction occurred on the non-shape-selective external surface or in the pore entrances. However, the evidently higher selectivity of 2,6-DIPN isomerization to 1,6-DIPN than to 2,7-DIPN achieved on the HB and HM than on the ASA catalyst (Table 2) indicates a shape-selectivity effect. A careful comparison of the ratio of 1,6-DIPN to 2,7-DIPN obtained at low conversions (2,6-DIPN isomerization conversion $< 20\%$) for various catalysts also indicates participation of the pore entrances in the DIPN isomerization. The ratio of 1,6- to 2,7-DIPN in the product obtained over the HY zeolite is lower than 1 and is lower than that for the ASA catalyst (1.35 for 19% isomerization conversion). This suggests that part of the product was formed inside the pores of the HY zeolite. However, for the HM and HB zeolites, the ratio was significantly higher than 1 (2.2–2.5 and 2.1–3.6, respectively) and higher than that obtained with the ASA catalyst. It seems that such a high ratio over the HB catalyst did not follow the kinetics of isomerization on the non-shape-selective external surface. Any product of isomerization of 2,6-DIPN, originating from the interior of the zeolite crystallite (namely 2,7-DIPN), should further decrease the ratio. In such a case, a ratio similar to or smaller than that for the ASA catalyst can be expected for the zeolites (cf. the HY zeolite). Therefore, only the activity of the pore entrances in this reaction seems to be a reasonable explanation of the above incoherence. The 2,6-DIPN can easily penetrate the pores and pore entrances, and 1,6-DIPN can easily leave the pore entrances. Moreover, 1,6-DIPN is kinetically preferred, and in the case of the 2,6-DIPN molecule adsorbed in the pore entrance there is no steric hindrance in relation to the alkyl substituent outside the zeolite pore, and 2,6-DIPN can easily isomerize to 1,6-DIPN. The high maximum concentration of 1,6-DIPN (12–13%) observed in the product of isomerization of 2,6-DIPN over the HB zeolite (Fig. 2C) is also noteworthy; it is higher than those obtained over other catalysts (10–11%) or that predicted by thermodynamic equilibrium [4,6,22].

It is known that dealumination of mordenite catalysts and deactivation of the external surface enhanced the shape selectivity in the alkylation of naphthalene to DIPN [2,6,7,9–13]. However, even in the product obtained over very selective mordenites a relatively high content of 1,6-DIPN was observed [6,9,10]. Such a product contained 60–70% 2,6-DIPN, 20–30% 2,7-DIPN, 5–10% 1,6-DIPN, and only traces of other DIPN isomers. This relatively high concentration of 1,6-DIPN in alkylation products can be attributed to secondary isomerization of 2,6-DIPN occurring on the non-shape-selective external surface of the zeolites or in the pore entrances. However, in the case of the non-shape-selective external surface, a large amount of 1,7-DIPN would also be formed from 2,7-DIPN, that is, ca. 2–4%, if the isomeric product contained 5–10% 1,6-DIPN and ratios between the product isomers (1,6- and 1,7-) and between the starting isomers (2,6- and 2,7-DIPN) were similar. Other DIPN isomers can also be expected in the product formed on the non-shape-selective surface in amounts comparable to that of 1,6-DIPN (predicted by thermodynamics or kinetics). Therefore, a more rational explanation of this abnormally high content of 1,6-DIPN than catalysis on the non-shape-selective external surface is reactions occurring in the pore entrances. 1,6-DIPN probably better fits the void space in the pore entrances of mordenite than do 1,7-DIPN and other DIPN isomers.

It is also probable that the results of Kikuchi et al. [6] for DIPN adsorption on H-mordenite confirm the superior fitting of the 1,6-DIPN molecule in the pore entrances, which is even better than that of 2,7-DIPN. As can be seen from Fig. 6 in [6], 2,6-DIPN was adsorbed very quickly, but subsequently the amount of adsorbed 2,6-isomer decreased very slowly with time. Simultaneously, the uptake of 1,6-DIPN was quite noticeable, whereas that of 2,7-DIPN was several times slower. We may speculate that the 2,6-DIPN molecules filled the pores of mordenite very quickly and that they were then displaced from the pore entrances by 1,6-DIPN.

4.3. *Role of the pore entrances in the isomerization of 1,7-DIPN*

In the isomerization experiments with 1,3-DIPN and 1,7-DIPN we can assume that, apart from less important secondary reactions, most of the reactions occurred on the external surface of the zeolites. The external surface area of the tested zeolites is significantly smaller than the total surface area of the ASA (Table 1). Therefore, it is understandable that the ASA catalyst has a higher activity than the zeolites. The isomerization conversion of 1,3-DIPN was considerably lower for all zeolites, but the isomerization conversion of 1,7-DIPN was evidently lower only over the HM zeolite. In the reactions carried out over the HY and HB catalysts the isomerization conversion of 1,7-DIPN was certainly lower than that over the ASA catalyst, but the difference was not as dramatic as one might expect. In the case of the HB zeolite in particular, an even higher isomerization conversion was achieved (for 6 h) than over the ASA. A higher reactivity of 1,7-DIPN in experiments carried out on the HY and HB zeolites than on the ASA is evident if we compare results at the same conversion level (Table 3). The unusual ability of the HB zeolite to isomerize 1,7-DIPN, relative to the ASA catalyst, is also visible for a similar conversion level

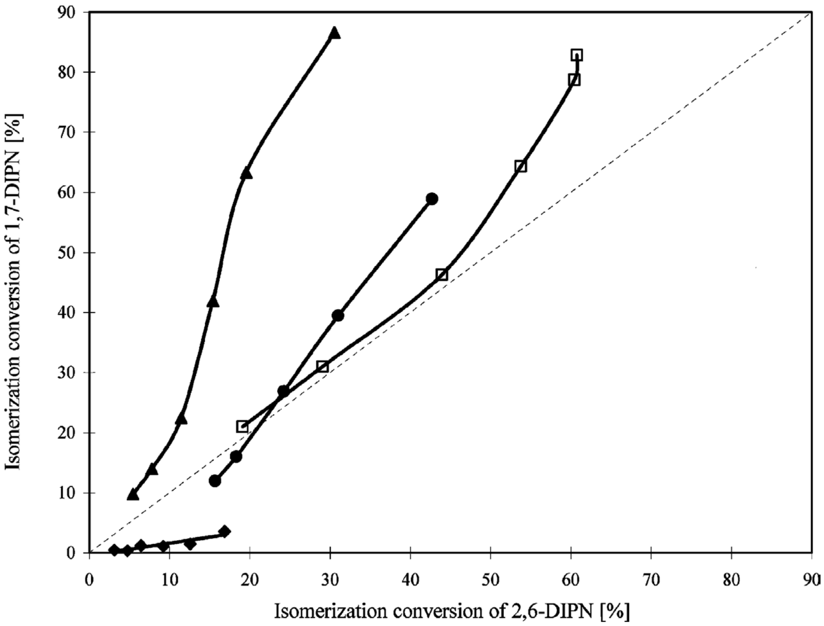


Fig. 5. Correlation between the conversion in isomerization of 1,7-DIPN and of 2,6-DIPN for different catalysts: □, ASA; ◆, HM; ▲, HB; ●, HY.

of intermolecular isomerization of DIPN. For instance, 63% isomerization of 1,7-DIPN was observed for the HB zeolite after 2 h (Fig. 4C), whereas only 46% was observed for the ASA after 0.5 h (Fig. 4A). Similar levels of isomerization of 1,3-DIPN (2%) and of the sum of 1,3-DIPN, 1,4-DIPN, and 2,3-DIPN (67%) were then observed for the two catalysts. These results confirm the shape-selectivity effects in the reactions of 1,7-DIPN occurring on the external surface of the HB zeolite.

A comparison of the activities of zeolites in relation to the individual DIPN isomers with various molecular sizes can cast some light on the problem of which part of the zeolite crystal participates in reactions of DIPNs. For 1,3-DIPN the comparison seems rather obvious, because the activity of all zeolites was very weak when compared with that of the ASA catalyst and is in accordance with the assumption of a small external surface area of the zeolites.

However, the comparison of the reactivities of 1,7-DIPN and 2,6-DIPN on different catalysts can supply us with some important information. Therefore, for the tested catalysts the isomerization conversions of 1,7-DIPN and 2,6-DIPN, obtained at respective recirculation times, are compared in Fig. 5. The dashed line represents a hypothetical catalyst on which equal isomerization conversions in the two isomerizations would be achieved. For the ASA catalyst the relationship was initially close to but slightly above the hypothetical line and indicated that over the ASA catalyst 1,7-DIPN reacted slightly more intensively than 2,6-DIPN. This resulted from differences in the kinetics of the two isomerizations under given conditions; that is, the rate of isomerization of 1,7-DIPN to 2,7-DIPN was slightly greater than that of 2,6-DIPN to 1,6-DIPN and 2,7-DIPN. The distance between the ASA relationship and the hypothetical line increased with reaction time, and the ASA curve approached a value that can be calculated from the starting concentrations of the two isomers and those at thermodynamic equilibrium.

The line plotted for the HM zeolite is significantly below the hypothetical one, and it is obvious that isomerization of 2,6-DIPN was preferred over that of 1,7-DIPN. On the other hand, the relationship determined for the HB zeolite shows that a reactivity of 1,7-DIPN that is higher than that of 2,6-DIPN. The obtained curve clearly exceeded the hypothetical line and the relationship obtained for the ASA catalyst.

The relationship achieved for the HY zeolite showed initially a higher activity in the isomerization of 2,6-DIPN, but next the plot was above the hypothetical and ASA lines. In contrast to that for the HB zeolite, the relationship obtained for the HY catalyst is significantly lowered by the isomerization of 2,6-DIPN, which occurs inside the zeolite pores (compare the discussion on the ratio of 1,6-DIPN and 2,7-DIPN in Section 4.2). Therefore, we can assume that on the external surface and in the pore entrances of the HY zeolite, isomerization of 1,7-DIPN also occurred more intensively than that of 2,6-DIPN.

The higher activity of the external surface of the HB and HY zeolites in the isomerization of 1,7-DIPN than that of 2,6-DIPN indicates that shape-selectivity effects occur on the outer layer of wide-pore zeolite crystals. The 1,7-DIPN molecule is better shaped to fit the shape of the external surface (i.e., pore entrances) of beta and Y zeolites than 2,6-DIPN. So, the 1,7-DIPN molecules have easier access to the active sites placed there and are more quickly consumed in reactions. In the case of mordenite, the 1,7-DIPN molecule does not match the shape of the void spaces on the external surface as well as 2,6-DIPN. Over mordenite 2,6-DIPN can also isomerize inside the pores, but the high excess of 1,6-DIPN over 2,7-DIPN indicates that this occurs only to a small extent.

5. Conclusions

It can be concluded that in the isomerization of DIPN the function of the external surface of zeolite crystals on the quality of the product can sometimes be more important than that of the interior of the pores. Even in the case of the isomerization of 2,6-DIPN, the abundance of 1,6-DIPN in the product indicates that the external surface participates efficiently in the reaction. A catalytic function of the interior of the zeolite pores was clearly visible only on the HY catalyst.

Some observations, such as the higher distribution of 1,6-DIPN than of 2,7-DIPN in the product of isomerization of 2,6-DIPN, performed on the H-mordenite and H-beta zeolites, and, unexpectedly, the higher isomerization rate of 1,7-DIPN than of 2,6-DIPN on the external surface of the H-beta and HY zeolites, indicate shape selectivity. Only the concept of catalysis in pore entrances seems to reconcile the shape-selectivity effects with the reactivity or formation of bulky DIPN isomers.

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