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Ring opening of decalin over zeolites
II. Activity and selectivity of platinum-modified zeolites

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Abstract

The activity and selectivity of platinum-modified zeolites (Beta, Y, Mordenite) were investigated in the ring opening of decalin at 473–543 K in the presence of hydrogen. In the course of decalin transformation, skeletal isomerization, stereoisomerization, ring opening, and cracking took place. The presence of platinum resulted in an enhancement of isomerization and ring-opening rates, as compared to the proton-form zeolites. The isomerization and ring-opening rates increased 3 and 5 times, respectively. Hydrogen pressure was found to suppress the secondary reactions and to prevent the catalyst deactivation. The isomerization and ring-opening reactions were not affected by hydrogen presence. Variations in catalyst deactivation were observed and attributed to different locations of organic deposits. Interactions between platinum and Brønsted acid sites suggested that the platinum crystallites were located partially in the channels of the studied zeolites. As a result of these interactions, the strength of Brønsted acid sites was reduced and consequently less cracking products were formed, at comparable conversions, over platinum-modified zeolites than over the corresponding parent zeolites.

Keywords: Ring opening; Isomerization; Zeolite catalysts; Platinum; Decalin; Acidity

1. Introduction

Environmental concerns have become nowadays the main driving force for the development of new and the modification of old refinery technologies. The minimized impact of the technologies on the environment and their sustainability are the main assets in the competitive environment of clean fuel production. As the diesel fuel has grown into the most wanted transportation fuel [1] because of the higher combustion efficiency of the diesel engines, its production capacity needs to be increased. At the same time new stricter legislative limits for diesel fuel composition, ensuring decreased emissions of harmful exhaust gases, have emerged [2]. These trends present a challenge for the industry: more diesel fuel must be produced and, at the same time, its quality must be improved. This poses high requirements on advanced fuel upgrading and ultimate utilization of the available raw materials.

The middle distillate fractions from secondary refinery processes, such as light cycle oil (LCO) originating from fluid catalytic cracking (FCC), have the potential of being a suitable component, to be blended in the diesel pool, in case these are further upgraded, so they do not deteriorate the diesel quality. Advanced refinery technologies, such as deep hydrodesulfurization and dearomatization [3], must be implemented in order to fulfill the limits for sulfur and aromatic contents, respectively. Cetane number (CN), another very important qualitative parameter of diesel fuels, which has been shown to be related to the improved quality of diesel emissions [4–7], can be increased by dearomatization

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as well. However, the enhancement may not be sufficient, as the CN of naphthenes is rather low, and additional upgrading may be needed [8]. The ring opening of the naphthenic ring is a promising option for achieving high cetane number values. Several patents, concerning diesel upgrading and ring opening, which have been recently issued, demonstrate the industrial importance of the ring opening [9–14].

Ring opening of naphthenes can be accomplished principally via two catalytic pathways: metal-catalyzed hydrogenolysis and acid-catalyzed cleavage of endocyclic carbon–carbon bonds in naphthenic rings. The basic principles of hydrogenolysis over metals have been recognized, while studying the isomerization of alkanes on metals [15]. The differences in the product distribution of the hydrogenolysis of naphthenes between Pt, on one hand, and Ir and Rh, on the other hand, have been ascribed to the differences in the mode of adsorption of cyclic hydrocarbons on these metals [15–17]. Results of catalytic experiments indicate that naphthenes adsorb either perpendicularly to the metal surface (e.g., on Ir, Rh), resulting consequently in the selective cracking of the secondary–secondary carbon–carbon bonds, or parallel to the metal surface (e.g., on Pt), assuring hydrogenolysis of any carbon–carbon bond and leading therefore to statistical distribution of the ring-opening products (ROP) [15]. Furthermore, the importance of Pt dispersion on the mode of adsorption has been identified. Statistical distribution of ROP has been observed on well-dispersed Pt whereas hydrogenolysis on Pt films resulted in similar distribution of products as in the case of ring opening over Ir. It has been concluded from the distribution of ROP that on Pt particles of 10–20 nm both mechanisms take place simultaneously.

The ring opening of five-membered-ring has been reported to be significantly faster than the ring opening of six-membered-ring naphthenes [15,18–20]. The effects of the structure of naphthenes on the rate and the selectivity of their hydrogenolysis over different metals have been investigated by McVicker et al. [20]. Ir was found to be the most active and selective for the ring opening of unsubstituted C–C in five-membered-ring naphthenes [20,21]. However, the ring-opening rates over Ir decreased substantially with the increasing number of alkyl substituents and were directly proportional to the number of secondary–secondary C–C bonds [20]. Although Pt was much less active than Ir, it showed, as a consequence of the multiplet mechanism, higher activity in cleaving the substituted ring C–C bonds. The importance of the *cis*/*trans* ratio of alkyl-substituted cyclopentanes for the parallel adsorption on Pt was reported as well. The ring-opening rates were decreasing with the increasing concentration of the *trans*-isomer.

The acid-catalyzed ring opening of naphthenes proceeds via cleavage of the corresponding carbocations. The reactions of carbocations attracted much attention and have been described in the literature based on the results of both experimental [22–24], and theoretical [25,26] studies. Recently, our group has applied these principles for the description of the ring opening of decalin over proton-form zeolites [27].

The benefits of the use of bifunctional catalysts, such as metals supported on zeolites, have been reported by several authors [18–20]. The acidic function promotes the isomerization of six-membered-ring structures into the five-membered, facilitating consequently the ring opening on the metal function. Investigations of more complex reaction systems, which would better represent the situation faced with real diesel feed, have been reported rather scarcely [27–31]. Arribas and Martínez [31] have shown that the yield of ROP from various diaromatics over Pt-modified zeolites and MCM-41 is temperature dependent. The channel structure and the strength of acid sites have been shown to play an important role in suppressing the undesired cracking reactions [31].

The present study investigates in detail the impact of Pt introduction into H-Beta, H-Y and H-Mordenite zeolites on their activity and selectivity in the ring opening of decalin. The influence of reaction temperature and hydrogen pressure on the course of the reaction is discussed as well.

2. Experimental

2.1. Catalyst preparation and characterization

The NH_4-Y (CBV712, $a_0 = 2.435\,\text{nm}$), NH_4-Beta (CP814E), and NH_4-Mordenite (CBV21A) zeolites were obtained from Zeolyst International. The NH_4-Y, Beta, and Mordenite zeolites were transformed to the corresponding proton forms through a step calcination procedure in a muffle oven at 773 K. The prepared proton-form zeolites were impregnated with a solution of hexachloroplatinic acid to obtain a loading of platinum on the zeolites equal to 2 wt%.

The specific surface area of the fresh and used Pt/H-Beta, Pt/H-Y, and Pt/H-Mordenite catalysts was measured by the nitrogen adsorption method (Sorptometer 1900, Carlo Erba Instruments). The coke content was determined as the carbon content on the spent catalysts (CHN-2000, LECO Corporation). The dispersion measurements were performed with a Coulter Omnisorp 100CX gas adsorption apparatus using the static volumetric adsorption method. The acidity of the investigated samples was measured by infrared spectroscopy (ATI Mattson FTIR) by using pyridine ($\geqslant 99.5\%$, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The state of Pt was determined by the XPS method (Perkin–Elmer 5400 ESCA). Further details on the catalysts characterization are reported in the supporting information.

2.2. Catalytic activity measurements

A mixture of decalin (bicyclo[4.4.0]decane) isomers (Fluka, $\geqslant 98\%$) with a *cis*-to-*trans* ratio of 2 to 3 was used as a starting material. The experiments were performed in

Table 1
Physical properties of fresh and used catalysts, conditions: 523 K, 2 MPa, and 360 min

Catalyst	SiO_2/Al_2O_3 (mol/mol)	Specific surface area			Carbon content (wt%)	Pt content (wt%)	Pt dispersion (%)	Pt mean particle size[a] (nm)
		Fresh (m^2/g)	Used (m^2/g)	Decrease (%)				
H-Beta	25	807	461	43	21.6	–	–	–
H-Y	12	1218	496	59	13.1	–	–	–
H-Mordenite	20	605	87	86	6.4	–	–	–
Pt/H-Beta	25	752	456	39	9.9	2	33	3.4
Pt/H-Y	12	960	590	39	10.8	2	58	2.0
Pt/H-Mordenite	20	590	254	57	5.4	2	33	3.4

[a] Assuming spherical particles.

an electrically heated 300-ml stainless-steel autoclave (Parr Industries) in the presence of hydrogen (99.999%) or argon (99.999%) in the kinetic regime. The study of the influence of the reaction temperature was carried out at 473–543 K and 2 MPa. The hydrogen partial pressure was in the range of 1.5–1.9 MPa under the reaction conditions. The influence of hydrogen pressure was investigated by varying the hydrogen partial pressure in the range 0.7–3.7 MPa while maintaining the temperature at 523 K. The liquid reaction products were analyzed with a gas chromatograph (Agilent 6890N) equipped with a capillary column (DB-Petro 100 m × 0.2 mm × 0.5 µm) and a FI detector. The GC/MS was applied to identify the reaction products. Additional details of the experimental procedure and product analysis can be found in supporting information.

3. Results and discussion

3.1. Catalyst characterization

The SiO_2/Al_2O_3 molar ratio of the investigated zeolites given by the manufacturer is reported in Table 1. Further characteristics of the zeolites can be found elsewhere [32]. The specific surface areas of fresh and spent catalysts determined by N_2 adsorption are summarized in Table 1 as well. All of the catalysts have very large specific surface areas (600–1200 m^2/g) calculated by the Dubinin method. For the spent catalysts, a reduction of their specific surface areas is observed. The surface area of the spent proton-form catalysts is reduced more than the area of the corresponding platinum-impregnated zeolites. Nevertheless, with the exception of Pt/H- and H-Mordenite, the surface areas of the spent catalysts remain fairly high (over 400 m^2/g) after 6 and 9 h reaction, respectively, at 523 K. The main reason for the decrease of the surface area is the blockage of pores by large hydrocarbon molecules and carbon deposits, as suggested by the comparison of the decrease in the specific surface area on one hand and the carbon content of the catalyst on the other hand (Table 1). The most prominent decrease of the surface area is found for H-Mordenite followed by H-Y and Pt/H-Mordenite (Table 1).

Table 2
Brønsted and Lewis acidity of fresh catalysts

Catalyst	Brønsted acid sites (µmol/g)			Lewis acid sites (µmol/g)		
	523 K	623 K	723 K	523 K	623 K	723 K
H-Beta	269	207	120	162	128	113
H-Y	255	205	129	123	75	58
H-Mordenite	331	284	212	71	50	39
Pt/H-Beta	316	199	0	82	15	0
Pt/H-Y	237	14	0	26	2	0
Pt/H-Mordenite	262	119	0	10	3	0

The Brønsted and Lewis acidities of the studied catalysts, as determined by pyridine adsorption (FTIR), are presented in Table 2. Significant difference between the proton-form zeolites and their platinum-impregnated counterparts can be observed. While the total amount of Brønsted acid sites (BAS), defined as the number of acid sites retaining pyridine at 523 K, is approximately the same for H and Pt/H zeolites, the concentration of the relatively strongest BAS, i.e., those able to retain pyridine at 723 K, decreases dramatically when the proton-form zeolites are impregnated with platinum (Table 2). Virtually no such sites are present in the platinum-modified zeolites. Moreover, the strongest Lewis acid sites (LAS) disappear after impregnation as well (Table 2). In contrast to BAS, the total concentration of LAS is substantially lower in Pt/H zeolites than in the respective H zeolites. The changes in the acid site strength distributions can be expected to be due to interactions between platinum crystallites and acid sites. Additionally, the distribution of acid site strengths is affected differently due to incorporation of platinum (Table 2), which is particularly obvious when comparing Pt/H-Beta and Pt/H-Y. This remarkable contrast can possibly originate from the structural differences between the zeolites, which may affect the interactions between platinum clusters and acid sites. Furthermore, the variation in the size of Pt crystallites (Table 1) may be important as well. Changes in product distribution, possibly due to the variation in the acid site strengths, are discussed in Section 3.5.

Several researchers have observed and studied the interaction between Pt and acid sites in zeolites [33–36] and have proposed theoretical explanations of this phenomenon based on the results provided by different catalyst characterization techniques [33–36]. The latest developments in the field have been reviewed by Stakheev and Kustov [36]. The support properties (e.g., acidity and basicity) have been shown to influence the electronic properties and crystallite morphology of supported metals. The changes in the properties of acidic and metallic sites have been also correlated with variations in activity and selectivity of these catalysts in several reactions, e.g., hydrogenolysis, isomerization, and hydrogenation [36].

The XPS characterization of Pt/H-Beta has shown that platinum was in the Pt^{2+} state, which is attributed to $PtCl_2$, prior to any treatment. Platinum chlorides are known to decompose during a prolonged XPS analysis and therefore the presence of other platinum chlorides in the dried catalyst cannot be resolved conclusively [37]. The platinum $4f_{7/2}$ binding energy (BE) of 73.3 eV, corresponding to the Pt^{2+} state, as observed for the impregnated catalyst, decreased to 71.8 eV as a result of platinum reduction. However, the BE of 71.0 eV, characteristic for the Pt^0 state, was not achieved. A similar shift in the binding energy of supported Pt, as compared to bulk Pt, was observed previously [38]. The differences in BE of bulk and supported metals, respectively, can be interpreted as a change in the electron density of the metal crystallites induced by interactions of metal with the support [33]. Furthermore, no traces of chlorine residues were detected in the reduced catalyst.

Due to the method used for Pt introduction (impregnation) the Pt crystallites can be expected to be located on the outer surface of the zeolites. This is confirmed by the average size of platinum crystallites (2–4 nm), as determined by hydrogen chemisorption (Table 1). If all platinum particles are located at the outer surface only, it would be far from the acid sites and there would exist no interactions between Pt crystallites and the acid sites. However, the lower acid site strengths (FTIR) of Pt zeolites as compared to their proton-form counterparts and the changes in the Pt^0 electronic state (XPS) indicate that at least part of the Pt crystallites is in the vicinity of the acid sites and thus inside the pores. Thus, keeping in mind that the size of crystallites from hydrogen chemisorption is an average value, it can be concluded that the platinum crystallites are located both inside the pores interacting with the acid sides (BAS and LAS) and on the outer surface as suggested by the chemisorption results. Nonetheless, for a deeper understanding of the catalytic system additional information about the distribution of platinum crystallite sizes would be helpful. This conclusion is further supported by the reaction data as discussed below.

3.2. Product analysis

The reaction of decalin led to a complex mixture of products containing more than 200 components. In order to facilitate the basic evaluation of kinetic results the products were grouped. The mixture of *trans*- and *cis*-bicyclo[4.4.0]decane is called decalin. Any C_{10} bicyclic structures other than decalin are referred as decalin isomers or simply isomers (Iso), and C_{10} monocyclic products, i.e., alkyl-substituted cyclopentanes and cyclohexanes, are denoted as ring-opening products (ROP). All products with a lower molecular weight than decalin are called cracking products (CP) and all products having more than 10 carbon atoms in the molecule and C_{10} aromatics are named heavy products (HP).

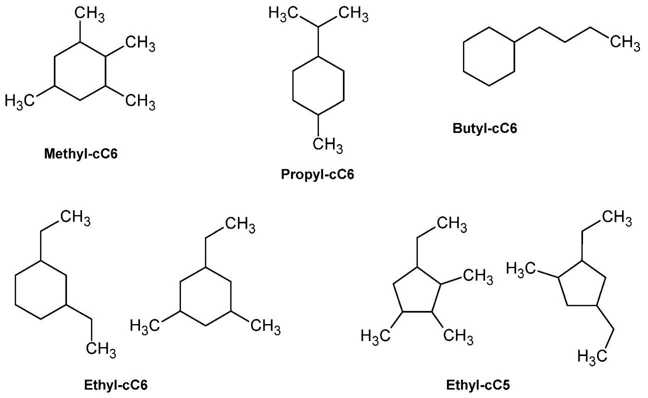


Fig. 1. Classification of ring-opening products into ROP groups and typical structures belonging to these groups.

The product identification was further refined by classifying ROP and Iso into subgroups by means of a pattern recognition method describing their mass spectra [39–43]. The following ROP groups were established: methyl-cC6, ethyl-cC6, propyl-cC6, butyl-cC6, and ethyl-cC5, where the first part of the name defines the longest alkyl substituent and the second part describes the size of the naphthenic ring, and unknown-ROP, which consists of all ROP that could not be classified into any other group. Typical structures of all ROP groups are given in Fig. 1. The organization of Iso into groups relies on the arrangement of the two naphthenic rings. Consequently, the following groups were created: methylbicyclo[4.3.0]nonanes, methylbicyclo[3.3.1]nonanes, dimethylbicyclo[3.3.0]octanes, dimethylbicyclo[3.2.1]octanes, trimethylbicyclo[2.2.1]heptanes, and unknown-Iso. All such isomers, which could not be classified into the first five isomer groups, belong to the unknown-Iso group. Some representative structures of the Iso groups are shown in Fig. 2. Full details on modeling of ROP and Iso classes, respectively, and classification of spectra of unknown compounds will be given elsewhere [44]. Major cracking products were identified as cyclic hydrocarbons C_5–C_9 and isobutane.

3.3. Initial activity of catalysts

The comparison of the initial activities of the investigated Pt catalysts is based on the total conversion of decalin after 20 min. As a consequence, the stereoisomerization of *cis*- to *trans*-decalin, which takes place at the same time, is not accounted for by the initial activity and will be discussed individually (Section 3.5.2). The addition of Pt into the proton-form zeolites results in a substantial increase of their initial activity (Fig. 3). The concentration of Brønsted acid sites, which has been shown to be essential for the activity of the

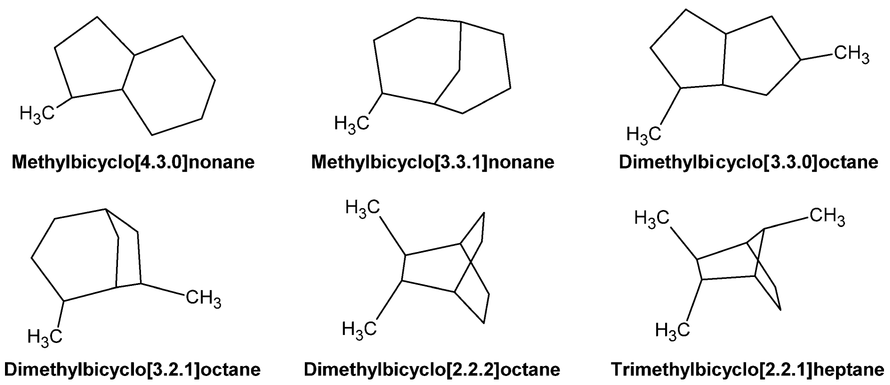


Fig. 2. Classification of isomers into Iso groups and typical structures belonging to these groups.

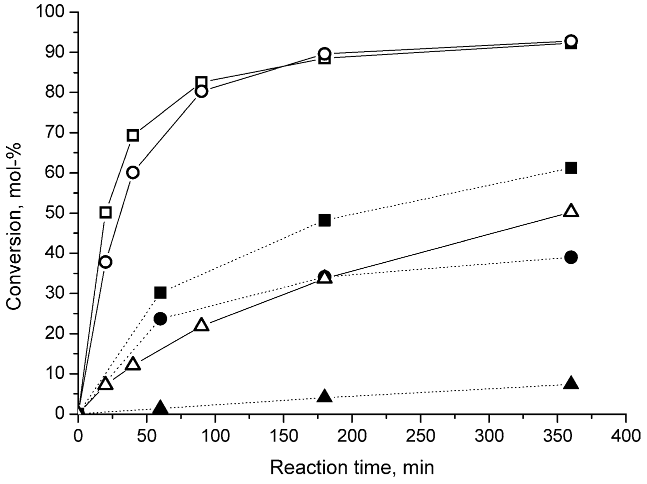
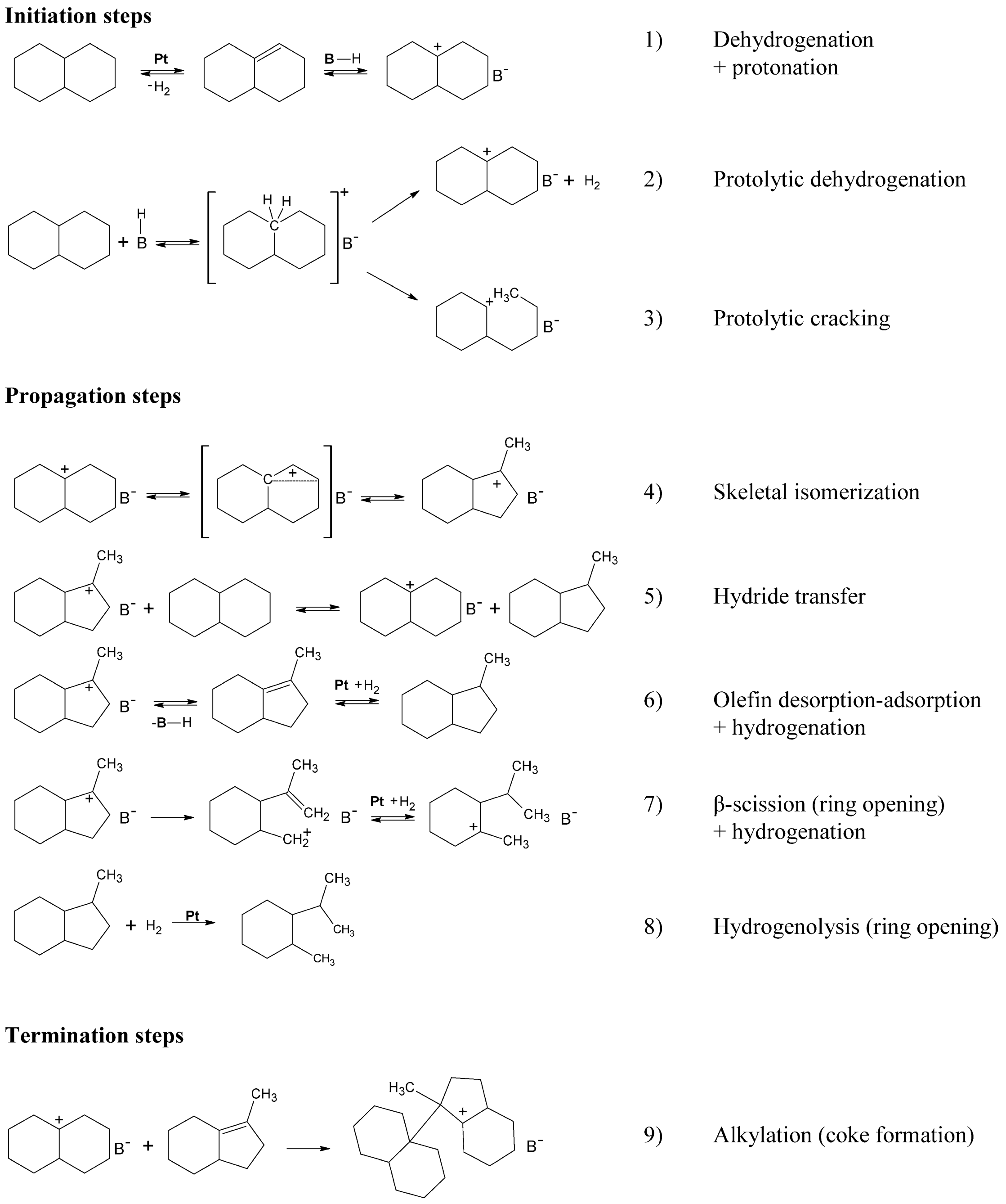


Fig. 3. Comparison of the activity of platinum-modified (open) and proton-form (filled) zeolites. Pt- and H-Beta (□, ■), Pt- and H-Y (○, ●), Pt- and H-Mordenite (△, ▲).

proton-form zeolites [27], does not increase by zeolites impregnation with Pt (Table 2). Therefore, the enhanced initial reaction rate can be unequivocally attributed to the presence of Pt. This implies that Pt facilitates the formation of reaction intermediates being subsequently transformed into products. In accordance with widely accepted principles of bifunctional catalysis [45–50], it can be suggested that Pt dehydrogenates decalin forming an olefin, which is in turn protonated by a Brønsted acid site. The produced carbenium ion can then undergo isomerization or ring-opening reactions (Scheme 1). As the Brønsted acid site is restored, an olefin is formed and hydrogenated on Pt to yield an isomer or a ring-opening product (Scheme 1). This mechanism is depicted, in a simplified form, in Scheme 1. Furthermore, the ring-opening products can undergo the same sequence of reaction steps, i.e., dehydrogenation on Pt followed by protonation of the resulting olefin, as well. The formed carbenium ion can then undergo either isomerization resulting in isomers of the primary ROP or β-scission, which leads to the formation of cracking products. Neither isomerization nor ring-opening reactions were observed in our recent experiments using Pt-modified VPI-5, a material possessing virtually no BAS, confirming thus the importance of BAS for decalin isomerization. Only dehydrogenation of decalin was observed over Pt/VPI-5. It can be thus concluded that decalin transformation into isomers, ring-opening, and cracking products proceeds via a bifunctional mechanism in addition to the mechanism observed on the proton-form zeolites (Scheme 1). Furthermore, it is seen that isomerization is an essential step for the ring opening of decalin.

Differences among the individual zeolite structures, impregnated with Pt, can be found (Fig. 3); their initial activity decreases in the following order: Pt/H-Beta $>$ Pt/H-Y $>$ Pt/H-Mordenite. The same order of the initial activities of the catalysts has been observed for the proton-form zeolites as well (Fig. 3) [27]. The activity of Pt/H-Mordenite is lower than expected from its chemical properties (Pt content, BAS concentration), as compared to Pt/H-Beta and Pt/H-Y zeolites. Recently, Arribas et al. [51] have explained the low yields of ring-opening products from tetralin over Pt/H-Mordenite (one-dimensional pore system) as compared to platinum-modified Beta and USY (three-dimensional pore system) by the differences in the zeolite structure dimensionalities. Previously, a lower activity of H-Mordenite in ring openings, as compared to H-Beta and H-Y, has been observed and explained by rapid blockage of the zeolite channels resulting consequently in very fast catalyst deactivation [27], which may be attributed to the lower pore dimensionality of H-Mordenite as compared to H-Beta and H-Y zeolites. Comparison of deactivation of the Pt-modified zeolites, on one hand, and of the relevant proton-form zeolites, on the other hand, will be presented below. Furthermore, experiments with Pt/H-Beta and Pt/H-Y reduced at 523 K disclosed that the catalysts activity and selectivity were independent of the reduction temperature.

The initial activity of the screened catalysts increases while elevating the reaction temperature (supporting information, Fig. 1A). However, it remains practically unaltered when the hydrogen pressure is increased from 0.7 to 3.7 MPa (supporting information, Fig. 1B). It can thus be concluded that hydrogen does not affect the initial rate of the reaction. Consequently, ring opening of decalin can be described as a zero-order reaction with respect to hydrogen. This conclusion has been verified by an additional exper-



Scheme 1. Proposed reaction scheme for isomerization and ring opening of decalin over bifunctional catalysts.

iment where hydrogen was replaced by argon. The substitution did not influence the initial catalyst activity (supporting information, Fig. 1B) confirming that the initial rate of ring opening of decalin is independent of the hydrogen pressure. Nevertheless, the presence of hydrogen is essential for a stable catalyst performance, as shown below.

3.4. Catalyst deactivation

Changes in catalysts activities in the course of the reaction were observed and attributed to the catalysts deactivation. The deactivation of the catalysts was verified by two independent methods: specific surface area measurements of fresh and spent catalysts, and determination of carbon content on the spent catalysts. Differences in the deactivation patterns in ring opening over proton-form zeolites have been reported [27] and explained by the different rates of deactivation being dependent on the zeolite structure. A closer examination of Fig. 3 reveals a change in the deactivation behavior of Y zeolite. The differences in the catalysts activities, as observed for the proton forms of Beta and Y zeolite, disappear after their impregnation with Pt. This indicates that Pt suppresses the fast deactivation of Y zeolite, most probably due to preventing the formation of large molecules remaining trapped inside the cavities of Y zeolite, as witnessed in the case of H-Y. On the other hand, Pt/H-Mordenite exhibits the highest deactivation among the investigated catalysts.

Comparison of the carbon content and of the decrease of specific surface areas of the spent catalysts provides useful information on the location of the deposits causing the catalyst deactivation (Table 1). The carbon content decreases in the following order: Beta > Y > Mordenite for both H- and Pt-form zeolites (Table 1). On the contrary, the reduction of the surface area follows the reverse order (Table 1). This obvious discrepancy can be explained by different locations of the coke molecules or its hydrocarbon precursors. In the case of Mordenite the deposits can be expected to be located on the pore mouths, thus blocking the whole channel system. As a result, vast specific surface area is lost due to the deposition of only small amounts of coke. On the contrary, the deposits are building up gradually inside the pores of Beta zeolite leading to a less dramatic drop in the specific surface area. The large organic molecules or coke deposits, which may remain trapped inside the cavities in Y zeolite and thus close parts of the channel system, will, accordingly, lead to higher losses of accessible surface area than the same amount of deposits in Beta zeolite. However, the decrease of the surface area is lower than in Mordenite where the complete channel system is blocked due to its unidimensionality. As the trends are more profound for the proton-form zeolites (Table 1), it can be concluded that Pt prevents the formation of coke and its precursors. Dimers of decalin or its isomers were observed when analyzing the soluble fraction of deposits from the spent catalysts. Their concentration was considerably lower (3 to 10 times) over Pt-impregnated zeolites, as compared to the corresponding H zeolites.

The catalyst deactivation can be prevented or slowed down by carrying out the reaction under hydrogen atmosphere. The effect can be most clearly observed for Y zeolite, the activity of which is more sensitive to the coke or hydrocarbon deposits formation than that of Beta zeolite. While in the case of Pt/H-Beta zeolite just a minor loss of activity can be observed when hydrogen is replaced by argon, in the case of Pt/H-Y a dramatic loss of activity is witnessed (Fig. 4). The observed conversion over Pt/H-Y in argon atmosphere is close to that of H-Y, thus implicating that rapid deactivation takes place. It can be therefore concluded that hydrogen effectively suppresses the deactivation of Pt/H-Y zeolite. On the other hand, the beneficial effects of hydrogen on the reaction are not so profound owing to the higher stability of Beta zeolite; there is virtually no difference over H-Beta and only a small difference over Pt/H-Beta in the catalyst activities when hydrogen or argon, respectively, are used (Fig. 4). Nevertheless, variations in the product distribution, resulting from changes of the hydrogen pressure, can be found, as discussed below.

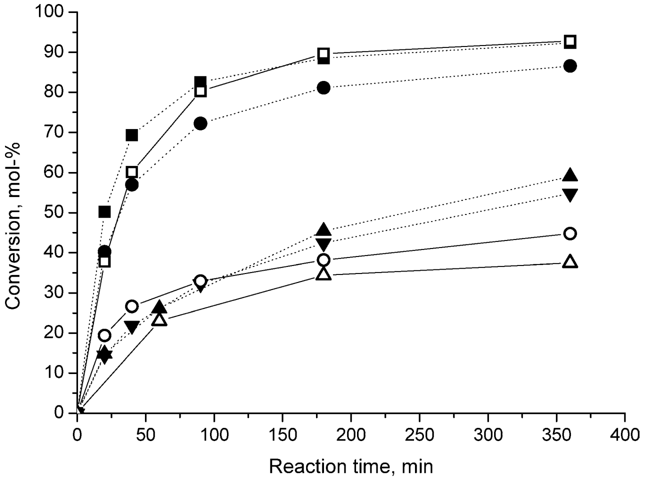


Fig. 4. Influence of reaction atmosphere on the activity of Pt- and H-Beta (filled) and Pt- and H-Y (open) at 523 K and 2 MPa overall pressure. Pt-, H_2 (■, □), Pt-, Ar (●, ○), H-, H_2 (▲, △) and H-, Ar (▼).

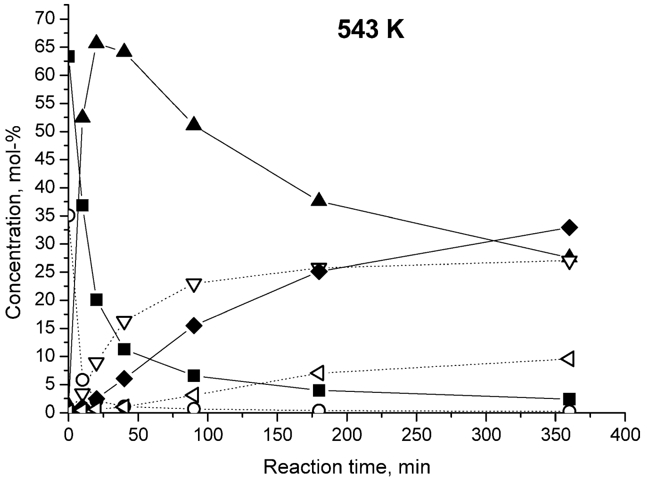
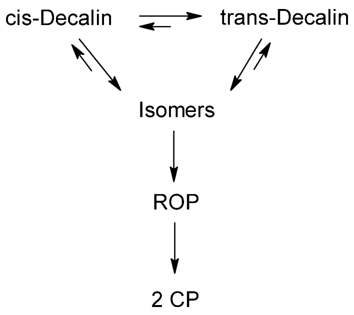


Fig. 5. Product distribution over Pt/H-Beta at 2 MPa, H_2, and 543 K. *Trans*-decalin (■), *cis*-decalin (○), isomers (▲), ring-opening products (▽), cracking products (◆), and heavy products (◁).

3.5. Distribution of reaction products

3.5.1. General product distribution

The time dependencies of the disappearance of *trans*- and *cis*-decalin, and of the formation of the reaction products, namely isomers (Iso), ring-opening products (ROP), cracking products (CP), and heavy products (HP), over Pt/H-Beta are depicted in Fig. 5 for 543 K. The concentration profiles obtained at 473 K (supporting information, Fig. 2) reveal that stereoisomerization of *cis*- to *trans*-decalin takes place and that it is faster, especially at lower temperatures, than the skeletal isomerization of any of the decalin stereoisomers. The stereoisomerization is quite facile and it is equilibrium driven, since once the equilibrium ratio of *trans*-to-*cis* isomer is reached, it does not change further. Conversely, the concentration profiles measured at 543 K (Fig. 5) disclose the details about decalin transformation into products, which cannot be observed at 473 K. Both decalin stereoiso-



Scheme 2. Simplified reaction scheme.

Table 3
The molar yield of products from decalin ring opening at 2 MPa and 473–543 K after 360 min

Catalysts	Isomers				Ring-opening products			
	473 K	493 K	523 K	543 K	473 K	493 K	523 K	543 K
Pt/H-Beta	26.0	61.3	42.0	27.5	0.6	8.3	30.2	27.0
Pt/H-Y	20.3	54.1	35.2	–	0.5	7.8	27.2	–
Pt/H-Mordenite	–	18.7	45.6	60.3	–	0.6	3.2	8.8

Catalysts	Cracking products				Heavy products			
	473 K	493 K	523 K	543 K	473 K	493 K	523 K	543 K
Pt/H-Beta	0.4	0.6	16.4	32.9	1.5	0.1	3.6	9.6
Pt/H-Y	0.1	1.9	26.3	–	1.0	0.2	4.1	–
Pt/H-Mordenite	–	0.1	1.1	3.2	–	0.1	0.3	0.8

mers are rapidly converted into skeletal isomers of decalin (Iso), which react further producing ring-opening products (ROP). Finally, the ROP undergo the undesired cracking reactions, yielding the cracking products (CP). Some of the CP (C_8 and C_9) originate from disproportionation reactions [52] and are accompanied by the formation of methyldecalins or their isomers. Parallel to the main course of the reaction, dehydrogenation, resulting in the formation of aromatics, may take place. This reaction pathway is more pronounced at low hydrogen pressures and at higher temperatures. The formed aromatics constitute, together with methyldecalins, a product group denoted as heavy products. The data can be well described by the proposed simplified reaction network for decalin conversion over proton-form zeolites (Scheme 2) [27].

The influence of temperature on the distribution of products over the investigated catalysts is reported in Table 3. The behavior of Pt/H-Mordenite, which showed a lower activity than Pt/H-Beta and Pt/H-Y, is clearly different from the other catalysts. Due to the low conversions achieved, rather low yields of CP, ROP, and HP are observed. Furthermore, yields of all products are increasing with the increasing temperature. This contrasts with Pt/H-Beta and Pt/H-Y, which show a maximum in the yield of Iso after 360 min (Table 3). The observed difference could be misleading if the product distribution is not considered at the same conversion level and thus such comparison is presented in the sequel. In the case of Pt/H-Beta a decrease in the yield of ROP is witnessed when increasing the reaction temperature from 523 to 543 K (Table 3). This clearly demonstrates that, dependent on the catalyst activity, an optimum temperature range exists, in which the maximum yield of ROP can be achieved. Moreover, the data in Table 3 indicate that the activity of the catalyst is not the only criterion determining the product distribution, as there are differences in the product distribution over Pt/H-Beta and Pt/H-Y, even though they exhibited very similar activity at a given temperature and can be thus compared directly.

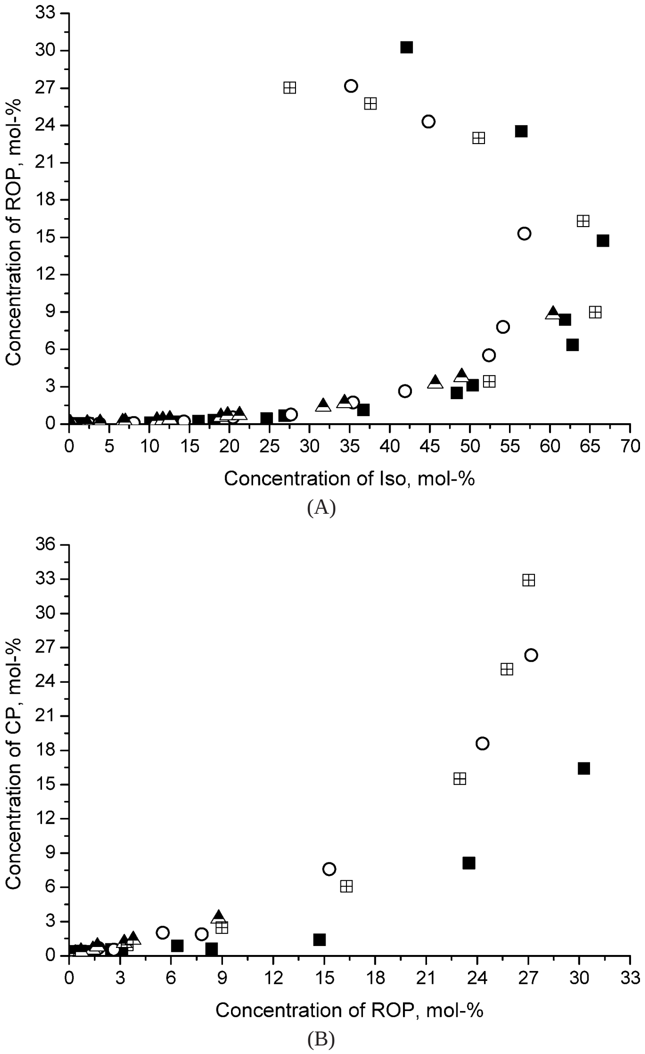
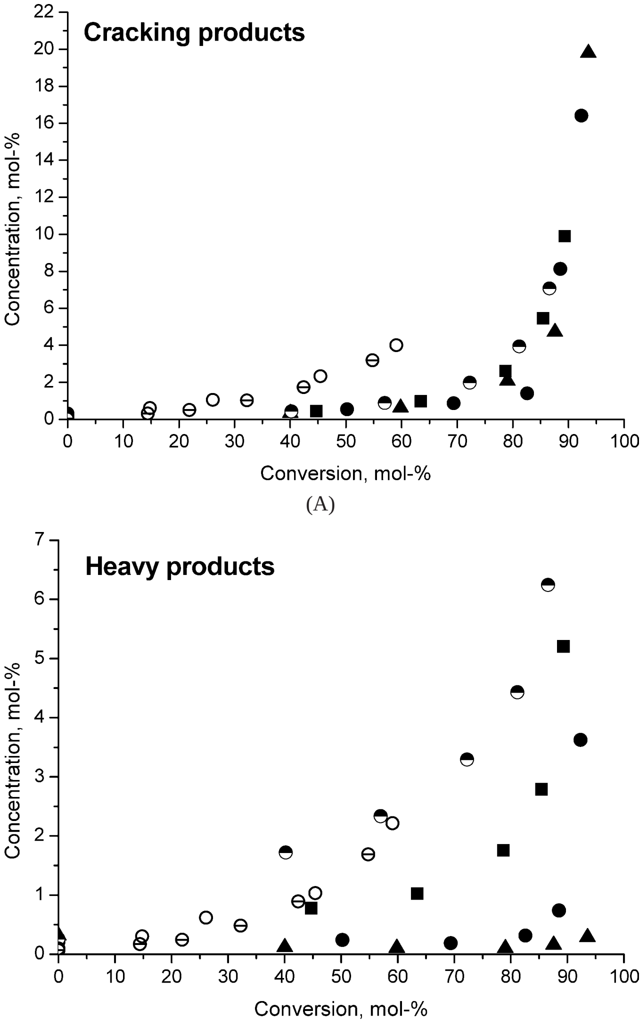


Fig. 6. Comparison of ROP formation as a function of isomer concentration (A) and cracking product formation as a function of ROP concentration (B) for Pt/H-Beta (■), Pt/H-Y (○) and Pt/H-Mordenite (▲) at 2 MPa, H_2 and 473–523 K. Data for Pt/H-Beta at 543 K are highlighted by (⊞).

The distribution of products is affected, at a comparable conversion, generally only to a minor extent by temperature (supporting information, Fig. 3). Nevertheless, a comparison of the formation of ROP from Iso (Fig. 6A), and CP from ROP (Fig. 6B) over Pt/H-Beta at 523 and 543 K, respectively, provides evidence of the temperature influence on the product distribution. It can be seen that the higher temperature promotes both the conversion of isomers into ring-opening products (Fig. 6A) and the consecutive cracking of ROP (Fig. 6B). Fig. 6B reveals a certain similarity between Pt/H-Beta at 543 K and Pt/H-Y at 523 K, indicating that, at the same temperature, cracking is more favored over Pt/H-Y. This conclusion is further justified by the differences in the product distribution, which can be found when comparing Pt/H-Beta, on one hand, and Pt/H-Y, on the other hand. At comparable conversions, the lower yields of isomers over Pt/H-Y are accompanied by increased yields of cracking products, as compared to Pt/H-Beta (supporting information, Fig. 3). At the same time, practically the same yields of ROP and HP, respectively, are observed for both catalysts. The difference indicates that the ring-opening activity of Pt/H-Y exceeds that of Pt/H-Beta. As the yield of ROP remains, however, unaltered and instead the yield of CP increases, it can be concluded that Pt/H-Y possesses also a higher cracking activity than Pt/H-Beta. This may seem surprising since similar concentrations of the acid sites and their strength distribution (Table 2) as well as similar Pt dispersions of both catalysts (Table 1) are observed. Furthermore, the smaller dimensions of Beta could be expected to favor recracking of the intermediate ROP while diffusing out of the pores. The dissimilarity in the product distributions can be tentatively attributed only either to different crystal sizes of Beta and Y zeolites or to differences in their external surface areas. Zeolite Beta is known for the Brønsted acid sites being present at its relatively large external surface, as compared to other zeolites [53]. These may be responsible for the formation of ROP which do not undergo successive recracking, thus resulting in a lower extent of cracking than over Pt/H-Y.

Hydrogen pressure is found to influence the product distribution (Figs. 7A and 7B and supporting information, Figs. 4A and 4B) even though it does not affect the activity of Pt/H-Beta (supporting information, Fig. 1B). While almost no effect of hydrogen pressure on the distribution of Iso, ROP, and CP can be observed, the distribution of HP (Fig. 7B) is affected substantially. The concentration of HP increases as the hydrogen pressure decreases. The highest yield of HP is observed when hydrogen is substituted by argon (Fig. 7B). Detailed analysis of the composition of the heavy products reveals that the decreasing hydrogen pressure enhances the formation of aromatics, mainly tetralin and methylindanes, thus resulting in higher yields of HP.

Comparison of proton-form and Pt/H-Beta, displayed in Figs. 7A and 7B and supporting information, Figs. 4A and 4B as well, shows that the product distribution is affected by the presence of Pt in the zeolite. Pt-modified Beta exhibits higher selectivity to desired products (ROP and Iso) due to the suppressed formation of by-products (CP and HP). The decreased formation of HP over Pt/H-Beta can be ascribed to the lower formation of aromatics owing to the hydrogenation activity of platinum (Fig. 7B). The decrease in the cracking activity of Pt/H-Beta, as compared to H-Beta, is more intriguing (Fig. 7A). Two concepts can be considered to explain this interesting phenomenon: lower cracking activity of Pt/H-Beta and hydrogenation of reaction intermediates prior to their cracking. In the latter case, Pt would reduce the concentration of active species on the surface, thus preventing their cracking. This would, however, mean that at the same time the concentration of ROP should be, at comparable conversion levels, higher over Pt/H-Beta than over its proton-form counterpart. This is not, however, the case since yields of both ROP and Iso (supporting information, Figs. 4A and 4B), respectively, are the same regardless of the presence of platinum. This indicates that the hydrogenation of surface intermediates cannot explain the observed difference in the product distribution over H-Beta and Pt/H-Beta.



(A)

(B)

Fig. 7. Concentration of reaction product groups for Pt/H-Beta and H-Beta at 523 K and various overall pressures, 1 MPa (■), 2 MPa (●, ○, ◓, ⊖), 4 MPa (▲). Pt-, H_2 (filled), Pt-, Ar (half-filled), H-, H_2 (open), H-, Ar (crossed). Product groups: cracking products (A) and heavy products (B).

The observed lower cracking activity of Pt/H-Beta, as compared to H-Beta, requires a closer look at the distribution of acid sites (Table 2) in order to explain the phenomenon. As seen from Table 2, the Pt-impregnated zeolites differ essentially from their proton-form counterparts in the concentration of the strongest acid sites, i.e., the sites retaining pyridine at 723 K. There are virtually no such sites present in Pt-impregnated zeolites. The decrease in the strength of the acid sites may be attributed to the interactions between Pt and acid sites. This type of interactions has been observed previously [33–36] and several theories explaining it have been proposed. Regardless of inclination to a particular theory, the change in electronic character of platinum due to the interactions with acid sites, observed by XPS as a shift in platinum binding energy (Section 3.1), may be related to the change in the character of acid sites determined by FTIR measurements. In this case, the change in the acid sites character evinces itself as the alteration of the acid site strength distribution.

Assuming that the strongest Brønsted acid sites are active mainly in cracking, the lower yield of cracking products over Pt zeolites can be explained by the absence of such acid sites in Pt/H-Beta. Nevertheless, it can be anticipated that a change in the acid sites strength will decrease the yield of ring-opening products as well, as both cracking and ring opening are catalyzed by BAS [27,28,30]. Moreover, the cleavage of exocyclic C–C bonds (i.e., cracking) is known to proceed at a much faster rate over bifunctional catalysts than the cleavage of endocyclic C–C bonds (i.e., ring opening) [54]. This indicates that the decreased strength of zeolite acid sites should influence the ring-opening reaction more than the cracking reactions. However, there are hardly any visible differences in the yield of ROP over H-Beta and Pt/H-Beta, respectively, at comparable conversions of decalin. This implies that some other active centers take part in the ring opening, thus compensating the decreased yield of ROP due to weaker Brønsted acid sites. The compensation of the ROP yield may be attributed to platinum itself since it is known as a catalyst active in hydrogenolysis [15,20]. The ring opening on platinum and on acid sites is discussed in detail below.

3.5.2. Stereoisomerization of decalin

Differences in the rate of consumption of *cis*- and *trans*-decalin, respectively, can be observed in the investigated temperature range (Fig. 5 and supporting information, Fig. 2). Data collected at temperatures above 513 K superficially indicate that *cis*-decalin is converted into skeletal isomers much faster than *trans*-decalin. However, inspection of data obtained at lower temperatures (supporting information, Fig. 2) reveals that the isomerization of *cis*-decalin to *trans*-decalin (decalin stereoisomerization) takes place under the investigated reaction conditions. The stereoisomerization is thermodynamically driven since once the equilibrium ratio of *trans*-to-*cis* decalin is reached only decalin conversion into the skeletal isomers can be observed. It can be thus concluded that the differences in the rate of consumption of *cis*- and *trans*-decalin are in fact due to the stereoisomerization; i.e., that the rates of skeletal isomerization of *cis*- and *trans*-decalin, correspondingly, are similar.

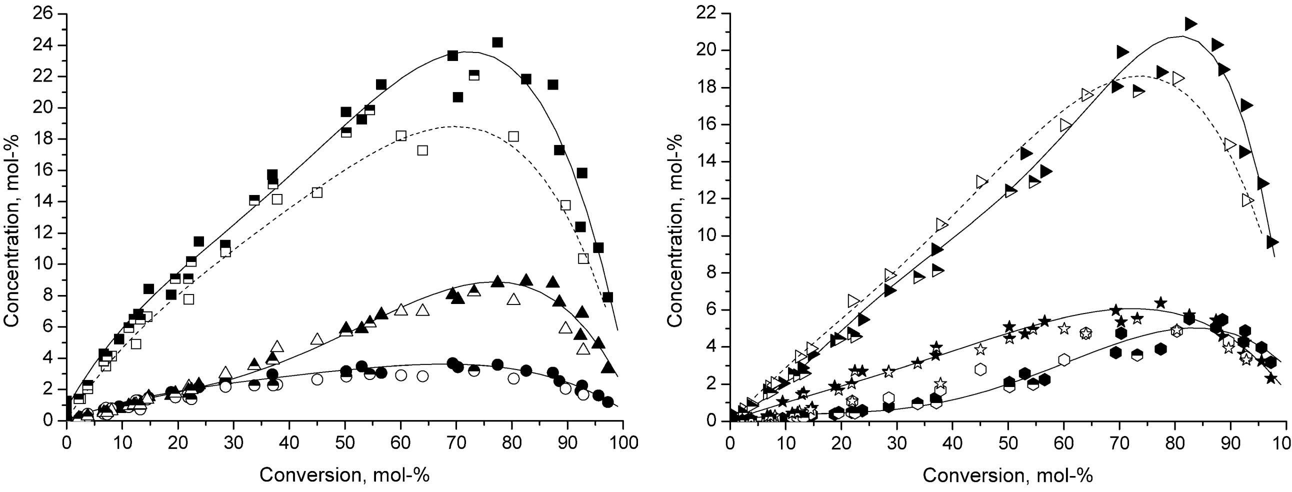
The stereoisomerization of decalin over Pt/H zeolites proceeds, in addition to stereoisomerization of decalin facilitated solely by acid sites [27], via the dehydrogenation–hydrogenation mechanism, as proposed by several authors [46,55]. The dehydrogenation–hydrogenation of decalin, resulting in decalin stereoisomerization, is favored over the decalin isomerization, catalyzed solely by the Brønsted acid sites, in the studied temperature range (Fig. 5 and supporting information, Fig. 2). The skeletal isomerization gains importance only when increasing the temperature.

3.5.3. Skeletal isomerization of decalin

The skeletal isomerization of decalin is an essential reaction step in decalin ring opening. It has been shown that the direct selective ring opening of the cyclohexane ring, which is present in decalin, is unfavorable [15,18,20,27]. The preferred reaction pathway includes the ring contraction of the stable cyclohexane ring to the cyclopentane ring that is more prone to ring opening. Moreover, it has been recently shown that the skeletal isomerization of decalin consists of several parallel and consecutive steps [27]. It can be anticipated that some of the isomers will undergo ring opening more readily than others. Therefore, the knowledge of the structure and abundance of the particular isomers is helpful for identification of the optimal reaction conditions, i.e., conditions under which the maximum yield of ring-opening products and, at the same time, the minimum yield of cracking products are attained.

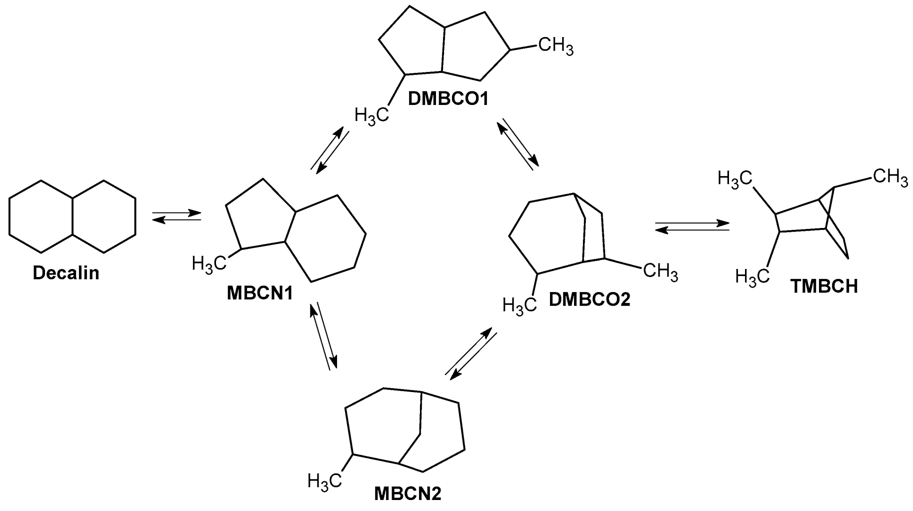
Isomers distribution over the studied catalysts in the investigated temperature range is compared at constant hydrogen pressure (1.7 MPa) in Fig. 8. The curves, representing the dependency of isomer-group concentrations on conversion, are in line with the proposed reaction scheme for decalin isomerization over proton-form zeolites (Scheme 3) [27]. According to this scheme, decalin first yields methylbicyclononanes via ring contraction, which can further react to form dimethylbicyclooctanes. In the end, trimethylbicycloheptanes are formed. This interpretation reflects the positions of the maximum of the individual isomers concentrations, and it is further supported by the characteristic S-shape curve for the concentration dependence of dimethylbicyclooctanes and trimethylbicycloheptanes on conversion. Due to the lack of mass spectral data for some types of isomers, e.g., trimethylbicyclo[3.1.1]heptanes or dimethylbicyclo[2.2.2]octanes, some of the isomers had to be denoted as unknown (Fig. 8B). Moreover, the group of unknown also contains such isomers that could not be chromatographically separated and their classification into one of the known groups was therefore doubtful. Hence the shape of the curve for unknown isomers cannot be interpreted unambiguously (Fig. 8B).

Neither temperature (Fig. 8) nor hydrogen pressure (supporting information, Fig. 5) have a major influence on the isomer groups product distribution, as it is revealed by a closer examination of the figures. At the same time, variations between the different zeolite structures can be found (Fig. 8). While there is virtually no difference between the distributions of isomers over Pt/H-Beta and Pt/H-Mordenite, the concentration of individual isomers over Pt/H-Y deviates from the pattern observed for Beta and Mordenite. As



(A) (B)

Fig. 8. Concentration of isomer groups as a function of decalin conversion over for Pt/H-Beta (filled), Pt/H-Y (open) and Pt/H-Mordenite (half-filled) at 2 MPa, H_2 and 473–543 K. Isomer groups: (A) methylbicyclo[4.3.0]nonanes (■, □, ⬒), methylbicyclo[3.3.1]nonanes (●, ○, ◓), dimethylbicyclo[3.3.0]octanes (▲, △, ◭), (B) dimethylbicyclo[3.2.1]octanes (▶, ▷, ⧐), trimethylbicyclo[2.2.1]heptanes (⬢, ⬡, ⬣), and not identified (★, ☆, ✭).



Scheme 3. Simplified reaction scheme of decalin skeletal isomerization. Products: methylbicyclo[4.3.0]nonanes (MBCN1), methylbicyclo[3.3.1]nonanes (MBCN2), dimethylbicyclo[3.3.0]octanes (DMBCO1), dimethylbicyclo[3.2.1]octanes (DMBCO2), trimethylbicyclo[2.2.1]heptanes (TMBCH).

this variation is witnessed already at low conversions (i.e., $< 50\%$), it cannot be ascribed to the lower yield of Iso over Pt/H-Y, which is observed only at conversions $> 50\%$ (supporting information, Fig. 3) and can be hence attributed to the differences in the individual isomerization steps.

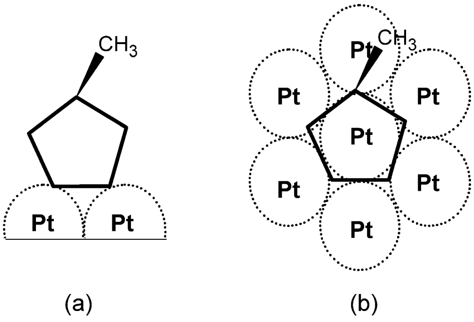
The formation of methylbicyclononanes, methylbicyclo[4.3.0]nonanes (MBC[4.3.0]N) and methylbicyclo [3.3.1]nonanes (MBC[3.3.1]N), is decreased over Pt/H-Y in favor of formation of methylbicyclooctanes, dimethylbicyclo[3.3.0]octanes (DMBC[3.3.0]O), and dimethylbicyclo-[3.2.1]octanes (DMBC[3.2.1]O), as seen in Fig. 8. Nevertheless, the trends are more profound for the more abundant isomers, i.e., MBC[4.3.0]N and DMBC[3.2.1]O. Previously a similar difference, only more pronounced, was reported for H-Beta and H-Y zeolites [27]. The difference has been linked to the different pore geometries of these catalysts since the other parameters, such as temperature and acidity, had been shown not to affect the isomers distribution [27]. Since the temperature and the acidity do not influence, to a major extent, the distribution of isomers and the catalysts contain the same amount of platinum, the variation in the concentration of methylbicyclononanes and dimethylbicyclooctanes, respectively, can be most probably assigned to the structural differences of Beta and Y zeolites. The structural differences are characterized by different channel sizes of Beta (0.76 × 0.64 and 0.55 × 0.55 nm) and Y zeolite (0.74 × 0.74 nm) [53]. Moreover, zeolite Y contains large supercages with diameters of 1.20 nm [53]. Both zeolites can accommodate decalin (0.69 × 0.50 nm) [28] and its isomers. Nevertheless, penetration of the smaller pores in Beta zeolites by decalin will probably be restricted by diffusional limitations.

Comparison of proton-form and Pt-impregnated Beta zeolite discloses that the distribution of isomers depends on the presence of platinum (supporting information, Fig. 5). On the other hand, no effect of substitution of hydrogen by argon on the distribution can be found, neither over H-Beta nor over Pt/H-Beta. This implies, together with the same distributions of isomers at various hydrogen pressures (supporting information, Fig. 5), that the isomerization of decalin is not dependent on hydrogen. The biggest difference between H- and Pt/H-Beta is found for the dimethylbicyclo[3.2.1]octanes, which are preferred over the Pt-modified Beta zeolite.

3.5.4. *Ring opening of decalin and isomers*

Ring opening of naphthenic hydrocarbons can be accomplished by hydrogenolysis on metals, such as Pt, Rh, Ru, and Ir [15,20], and on the solely acidic catalysts possessing sufficient concentration of Brønsted acid sites, e.g., zeolites [27–30]. The mechanisms of ring opening have been studied extensively only for the metal catalysts. It has been shown that the ring opening of five-membered hydrocarbon rings is favored to the ring opening of six-membered hydrocarbon rings [18–20]. McVicker et al. [20] have demonstrated this by using a series of unsubstituted bicyclic hydrocarbons. The conversion over 0.9% Ir/Al_2O_3 decreased in the following order: bicyclo[3.3.0]octane > bicyclo[4.3.0]nonane ≫ bicyclo[4.4.0]decane [20]. Furthermore, the same authors have shown that the rate of ring opening decreases for alkyl-substituted cyclopentanes with the increasing number of ring substituents, i.e., with the decreasing number of secondary–secondary C–C bonds [15,20].

Differences in the activity and selectivity to ring openings have been reported for different metals as well. Ir has been found to be the most active and selective in the ring opening of the unsubstituted C–C bonds in five-membered-ring naphthenes [20]. However, the increasing number of alkyl substituents reduces substantially the ring-opening rates over Ir catalysts. It has been demonstrated that the ring-opening rates over Ir catalysts were directly proportional to the number of secondary–secondary C–C bonds [20]. Contrary to Ir, Pt is much less active. However, it exhibits a higher activity in cleaving the substituted ring C–C bonds, which is a consequence of the multiplet mechanism (Scheme 4) occurring on Pt. Since the multiplet mechanism relies on adsorption of molecules parallel to the metal surface, the bond between secondary and tertiary carbon atoms can be cleaved in addition to cleavage of secondary–secondary C–C bonds. Another consequence of the adsorption parallel to the metal surface is that the ring-opening rates are dependent on the *cis*/*trans* ratio of alkyl-substituted naphthenes, namely the ring-opening rates decrease with increasing concentration of the *trans*-isomer [15,20].



Scheme 4. Schematic presentation of methylcyclopentane adsorption on platinum: (a) perpendicular adsorption (doublet mechanism), (b) parallel adsorption (multiplet mechanism) [15].

A mechanism for ring opening of decalin over acidic catalysts has been recently proposed [27]. It explains the observed product distribution in the ring opening of decalin using experimental results and theoretical calculations for transformation of alkanes in zeolites. The active species are the adsorbed carbenium ions, which undergo isomerization and scission, thus yielding skeletal isomers of decalin and ring-opening products, respectively [27]. In the present case, both hydrogenolysis by metal and ring opening by acid sites must be considered simultaneously since the catalysts possess metal and acid functions. Furthermore, the bifunctional nature of the catalysts in this study facilitates the adsorption of isomers (by formation of the corresponding cyclic olefins) on Brønsted acid sites, thus enabling their faster ring opening (Scheme 1, Section 3.3).

The results of ring opening over platinum-modified zeolites, i.e., over bifunctional catalysts, are summarized in Table 3 (see also supporting information, Fig. 3). It can be observed that the yield of ring-opening products increases with the increasing temperature over all investigated catalysts (Table 3). Since almost no ROP are formed at the beginning of the experiments when the concentration of decalin is at its maximum, it can be concluded that the ring-opening products are actually produced by ring opening of isomers. Moreover, the data, depicted in Fig. 8 and supporting information, Fig. 4, suggest that the rate of ring opening increases with the increasing degree of isomerization. The differences in the yield of ROP over various catalysts are only minor. A closer examination of Fig. 6 reveals, however, a difference between Pt/H-Y and Pt/H-Beta. At lower concentrations of Iso, more ROP is formed over Pt/H-Y than over Pt/H-Beta. However, as the concentration of ROP grows, more cracking is observed over Pt/H-Y. Similarly, an increase in temperature decreases the amount of ROP formed at a comparable concentration of Iso (Fig. 6). At higher temperatures the ROP are consumed by cracking and consequently their yield decreases. The optimum in the temperature dependence is for Pt/H-Beta at 523 K, as can be seen in Table 3.

The variation in the product distribution of ROP among the studied catalysts is only minor (supporting information, Figs. 6 and 7), which is due to the high isomerization activity of the investigated catalysts. The dominant ROP groups are methyl-cC6, followed by ethyl-cC6. A substantial amount of ROP remains unidentified, however, due to (a) overlapping of the peaks of known groups, which prevents classification of such peak into any group, and (b) formation of C_{10} alkyl-substituted cyclopentanes such as methyl-, propyl- and butyl-cC5, which could not be classified since not enough data are available for the definition of these groups. It has been found that the majority of unidentified ROP are due to formation of C_{10} alkyl-substituted cyclopentanes. The trends of the concentration curves for propyl-cC6 and butyl-cC6 (supporting information, Fig. 6) show the S-shape characteristic for products being consumed by a successive reaction. In this case the consecutive reactions are isomerization to another ROP and cracking.

3.5.5. Formation of undesired by-products

Two kinds of undesired by-products are formed during the ring opening of decalin: cracking products and heavy products. The formation of cracking products can be attributed to successive reactions of ring-opening products on the Brønsted acid sites. Once again, this is facilitated by formation of olefins on the Pt sites, which are more prone to adsorption (and reaction) on BAS than their saturated counterparts. The cracking of isomers can be omitted since mainly C_4–C_9 hydrocarbons are formed during cracking and virtually no bicyclic products with less than 10 carbon atoms in the molecule are found among the reaction products; i.e., the direct cracking of isomers would require simultaneous rupture of two carbon–carbon bonds. The cracking products consist of C_5–C_9 naphthenes and C_3–C_6 alkanes; neither aromatics nor olefins were detected (supporting information, Table 1). The most abundant CP are cyclohexane and methylcyclopentane and isobutane.

The comparison of Pt-impregnated zeolites is given in the supporting information, Table 1, for different reaction temperatures. The cracking is most severe over Pt/H-Mordenite. It is the only catalyst that yields more alkanes than naphthenes at 523 K. This observation is further supported by the highest concentration of C_3–C_5 hydrocarbons obtained over Pt/H-Mordenite (Table 3). The distribution of cracking products over Pt/H-Beta and Pt/H-Y are similar, just a small preference of Pt/H-Y for deeper cracking can be found (supporting information, Table 1). Besides the effects of the nature of the catalyst, an influence of the reaction temperature on the distribution of CP over Pt/H-Beta is shown in supporting information, Table 1, as well. Quite naturally at the same reaction time, the amount of smaller hydrocarbons, C_3–C_5, increases with the increasing temperature, and is accompanied by a decrease of naphthenic hydrocarbons (supporting information, Table 1).

The hydrogen pressure does not substantially influence the composition of cracking products, as can be observed in supporting information, Table 2, for Pt/H-Beta. Furthermore, the distribution of CP is not affected when replacing hydrogen by argon. Although the distributions of CP over H- and Pt/H-Beta do not differ, the interpretation is not very straightforward since lower conversions are achieved over the proton-form zeolites. In contrast to cracking, the formation of heavy products is influenced by the hydrogen pressure, as clearly seen from the data in supporting information, Table 2. While increasing the hydrogen pressure, the relative concentration of aromatics dramatically decreases. The substitution of hydrogen by argon has the same effect as low hydrogen pressure; i.e., more aromatics are formed. The relatively low concentration of aromatics formed over H-Beta (supporting information, Table 2), as compared to Pt/H-Beta, can be explained by the absence of platinum in the former catalyst. Thus, platinum acts as a dehydrogenation catalyst in the absence or at low partial pressures of hydrogen.

3.6. Comparison of proton-form and platinum-modified zeolites

The activity of proton-form zeolites is greatly improved when they are impregnated with platinum; the initial isomerization rate and the initial ring-opening rate increase from 1.20 and 0.04 mmol/(g min), respectively, observed for H-Beta at 523 K to 3.84 and 0.20 mmol/(g min), respectively, found for Pt/H-Beta at the same temperature. The increase in the isomerization rate can be attributed to more facile formation of protonated species, active in isomerization, due to decalin dehydrogenation over platinum followed by protonation by acid sites (Scheme 1). Consequently, the ring opening is promoted as well. Since the strength of acid sites is decreased by platinum impregnation, less cracking is observed, at comparable conversions, over Pt/H zeolites than over H zeolites (Table 2, Section 3.5.1). As Brønsted acid sites are active in ring opening [27], it could be expected that the decreased strength of BAS will lead to suppression of ROP formation. However, proton-form and platinum-modified zeolites yield, at comparable conversions, the same amount of ROP. Accordingly, other active sites are responsible for ROP formation in addition to BAS. Since Pt is known for its hydrogenolysis activity (Section 3.5.4), it may be expected that some of the isomers will undergo hydrogenolysis over Pt sites. Moreover, the formation of heavy products and deactivation are suppressed by the presence of platinum. The modification of zeolites by platinum does not, to a major extent, affect the relative composition of isomers, ring-opening, and cracking products, respectively.

4. Conclusions

The activity of platinum-modified H-Beta, H-Y, and H-Mordenite has been investigated in ring openings of decalin at 473–543 K in the presence of hydrogen. The ring opening of decalin over platinum-modified zeolites has been found to proceed via several intermediates including different skeletal isomers of decalin. The major findings can be summarized as follows.

The modification of proton-form zeolites with platinum has been found to enhance the catalyst activity. The initial isomerization and ring-opening rates were increased 3 and 5 times, respectively. Yields of ring-opening products as high as 30 mol% are achieved; ring openings of decalin over proton-form zeolites yielded just 8 mol% of ROP [27]. The initial rate enhancement can be explained by the change of reaction initiation. In addition to initiation by protolytic cracking over Brønsted acid sites, as observed for proton-form zeolites, bifunctional initiation takes place. It includes dehydrogenation of decalin to an olefin, which is in turn protonated by Brønsted acid sites. The formed protonated species can undergo isomerization and ring opening.

The product distribution is affected by addition of platinum as well; lower yields of cracking and heavy products are obtained, as compared to proton-form zeolites. The lower cracking activity of Pt-modified zeolites is a consequence of the lower strength of Brønsted acid sites in Pt zeolites. The decrease of BAS strength, in comparison to proton-form zeolites, is due to the interactions between platinum particles inside the zeolite channels and Brønsted acid sites.

Hydrogen pressure has been found to influence the amount of heavy products; less heavy products are formed while using higher hydrogen pressure. The initial rates of formation of isomers and ring-opening products remain, however, unaltered when hydrogen pressure is varied. Moreover, replacement of hydrogen by argon does not affect the initial isomerization and ring-opening rates. However, the catalysts tend to deactivate faster in the absence of hydrogen. The effect is more pronounced for Pt/H-Y; the conversion is nearly 3 times higher when hydrogen is present. On the other hand, the conversion over Pt/H-Beta is just ca. 10% lower when hydrogen is replaced by argon. This dissimilarity is explained by different deactivation mechanisms of Pt/H-Y and Pt/H-Beta, correspondingly.

The product distribution of isomers is similar for both proton-form and platinum-modified zeolites. On the contrary, the distribution of ROP over Pt-modified zeolites differs from the one observed for H zeolites; relatively more methyl-cC6 is formed. It can be explained by the platinum-promoting isomerization of ROP. The primarily created propyl-cC6 is, accordingly, converted into ethyl- and methyl-cC6.

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Supplementary material

The online version of this article contains additional supplementary material.

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