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Ring opening of decalin over zeolites
I. Activity and selectivity of proton-form zeolites

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Abstract

The activity of H-Beta-25, H-Beta-75, H-Y-12, H-Mordenite-20, and H-MCM-41 was investigated in the ring opening of decalin at 498–573 K in the presence of hydrogen. The catalysts activity and deactivation were correlated to their acidity determined by FTIR pyridine adsorption, pore structure, and surface area changes. Skeletal isomerization, stereoisomerization, ring opening, and cracking were the prevailing reactions taking place. Skeletal isomerization included several parallel and consecutive reactions resulting in a wide variety of products, which underwent ring opening, and subsequently cracking. Virtually no direct ring opening of decalin was observed; i.e., decalin must first be isomerized to alkyl-substituted bicyclononanes and bicyclooctanes to make possible its ring opening. The main products were grouped according to their structural features to evaluate the product distribution, which was influenced by catalyst acidity and pore structure. The initial activity of the catalysts increased with increasing acidity and reaction temperature, respectively. The deactivation of the investigated catalysts depended on their pore structure; H-Y was deactivated faster than Beta zeolites as it allowed the formation of large hydrocarbon intermediates inside the cavities.

Keywords: Ring opening; Isomerization; Zeolite catalysts; H-MCM-41; Decalin; Acidity

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1. Introduction

Concern for the environment is the major driving force in the development of new automotive fuel compositions. Maximum combustion effectiveness and minimum emissions of pollutants are the most important features required. The reduction of sulfur and aromatics in diesel fuel can be achieved by using current technologies (hydrotreatment, hydrocracking) [1]. Dearomatization as a result of these technologies not only decreases the amount of particulates in the exhaust gases but also improves other diesel fuel characteristics by lowering the density and increasing the cetane number (CN). The cetane number is a very important parameter for the quality of the combustion process and thus for the amount of pollutants emitted; high CN results in lower NO_x and particulate emissions [2]. However, the increase of CN due to hydrogenation of aromatics may not always be sufficient, as the CN of naphthenes is rather low, too. This is a problem particularly in upgrading highly aromatic fractions such as light cycle oil (LCO) from FCC. Opening of at least one of the naphthenic rings is necessary to obtain appropriate cetane numbers [2].

Two kinds of ring openings are distinguished. In a generic ring opening, ring-external C–C bonds formed due to the scission of an internal bond of a naphthenic ring are cracked and the molecular mass of the resulting products is thus less than that of the feed. On the other hand, in selective ring opening the molecular mass remains almost unaltered, as only internal C–C bonds of naphthenic rings are broken.

The ring openings of cyclohexane and methylcyclopentane on metals are the most thoroughly studied reactions [3]. At least two different mechanisms have been recognized: the dicarbene mechanism with molecules adsorbed perpendicularly to the metal surface and the multiplet mechanism, according to which the molecules adsorb flat on the metal surface. In the latter case, a statistical product distribution is obtained (e.g., over well-dispersed platinum), whereas the

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former one ensures selective cracking of C–C bonds between two secondary carbon atoms (e.g., over Ir, Rh).

Ring opening of C_6 naphthenes has recently been studied on metals supported on zeolites, which due to their acidity enhance the isomerization rate of six-membered to five-membered carbon rings, thus facilitating the ring opening [4,5]. McVicker and co-workers have carried out a comprehensive study on the ring opening of several alkyl-substituted C_6–C_{10} mononaphthenes [6,7] and showed the selective properties of Ir catalysts in ring opening of five-membered carbon rings and stressed the importance of non-branching ring contraction of substituted cyclohexane rings to assist ring opening. The ring-opening rates over Ir were found to decrease significantly with the extent of alkyl substitution and were directly proportional to the number of secondary–secondary C–C bonds. Contrary to iridium, the authors reported platinum to be more active in breaking the substituted C–C bonds. The rate of ring opening over Pt catalysts was, however, sensitive to the *cis*-to-*trans* ratio of methyl-substituted cyclopentanes and decreased with increasing *trans*-isomer concentration.

In contrast to metal-assisted ring-opening reactions, it is believed that on acid catalysts the ring opening of C_6 and C_7 naphthenes proceeds on Brønsted acid sites being initiated by protolytic cracking and followed by chain reactions of the carbenium ions formed [8–10]. The mechanisms of cracking and isomerization of alkanes over acid catalysts, which have been studied most extensively [11–15], can be applied to naphthenes having just saturated carbon–carbon bonds as alkanes. Besides the experimental work, the results of theoretical calculations confirming the feasibility of proposed elementary reactions, such as protolytic cracking, protolytic dehydrogenation, hydride transfer, and skeletal isomerization, β-scission, and alkylation of adsorbed carbenium ions have emerged [16,17].

Ring opening of more complex molecules containing two fused rings is investigated considerably less. Arribas and co-workers investigated the simultaneous hydrogenation and ring opening of 1-methylnaphthalene and tetrahydronaphthalene over Pt-modified Beta and Y zeolite catalysts in the liquid phase [18,19]. It was found that the yield of ring-opening products (ROP) was temperature dependent and that the secondary channel structure formed due to catalyst steaming enabled easier diffusion of ROP from the pores, thus preventing secondary cracking and dealkylation. Pt/MCM-41 was also suggested to be suitable for simultaneous hydrogenation and ring opening of diaromatics as it is mildly acidic and has uniform mesopores and high surface area. In consequence, the losses due to cracking are minimized and a good dispersion of platinum on the surface is achieved [20]. In the case of methylnaphthalene the main products obtained were alkyl-substituted benzenes. Tetrahydronaphthalene yielded decalin and its isomers as prevailing products. Nevertheless, no detailed information about the different ring-opening and decalin-isomer products was provided.

Cracking of decalin over medium-pore (10-membered ring, MCM-22, ZSM-5) and large-pore (12-membered ring, Beta, Y) zeolites has been studied by Corma et al. [21]. The medium-pore zeolites were significantly less active, indicating the difficulties of decalin to penetrate into them. The predominant products were, in addition to cracking products (C_2–C_6), C_{10} alkylbenzenes [21]. Mostad et al. proposed that cracking of decalin is initiated by hydride abstraction [22,23]. However, as the main focus of these studies has been decalin cracking, the selectivities toward different isomeric and ring-opening products have not been investigated.

The present work is focused on finding a relationship between the acidity and the structures of H-Beta and H-Y zeolites and H-MCM-41 as well as their activity and selectivity in ring opening of decalin, since this has not been reported so far. A reaction network for decalin transformation is proposed and the intermediates in decalin isomerization and ring opening are identified. Decalin is used as a representative molecule of dinaphthenes formed during hydrogenation of diaromatics in middle distillates.

2. Experimental

2.1. Catalyst preparation and characterization

The NH_4-Y (CBV712, $a_0 = 24.35$ Å), H-Beta (CP811E-75), 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 proton forms through a step calcination procedure in a muffle oven. The materials were calcined at 773 K. The Na-MCM-41 mesoporous molecular sieve was synthesized according to the procedures described elsewhere [24,25] with some modifications. Na-MCM-41 was transformed to NH_4-MCM-41 by the ion-exchange method using ammonium chloride solution. The H-MCM-41 catalyst was obtained by calcination of NH_4-MCM-41 at 773 K.

The determination of structure and phase purity of a Na-MCM-41 mesoporous molecular sieve was carried out by an X-ray powder diffractometer (Philips PW 1800). The specific surface area of the fresh and used H-Beta-25, H-Beta-75, H-Y-12, and H-Mordenite-20 catalysts was measured by the nitrogen adsorption method (Sorptometer 1900, Carlo Erba Instruments). The catalysts were outgassed at 473 K prior to the measurements and the Dubinin equation was used to calculate the specific surface area.

The acidity of 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 samples were pressed into thin self-supported wafers (10–12 mg/cm^2). Pyridine was first adsorbed for 30 min at 373 K and then desorbed by evacuation at different temperatures (523, 623, and 723 K) to obtain a distribution of acid site strengths. All spectra were recorded at 373 K with a spectral resolution equal to 2 cm^{-1}. Spectral bands at 1545 and 1450 cm^{-1}, respectively, were used to identify Brønsted (BAS) and Lewis acid sites (LAS). The amounts of BAS and LAS were calculated from the intensities of corresponding spectral bands by using the molar extinction coefficients reported by Emeis [26].

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 an electrically heated 300-ml stainless-steel autoclave (Parr Industries) in the presence of hydrogen. The study of the influence of the reaction temperature was carried out at 473–573 K and 2 MPa. The stirring rate and starting material-to-catalyst ratio were kept at constant values equal to 1500 rpm and 22 (w/w), respectively. The hydrogen partial pressure was 1.7 MPa, thus resulting in a hydrogen-to-decalin molar ratio of 1 to 13 under reaction conditions. The screened catalysts were crushed and the fraction below 63 µm was used in the experiments to suppress internal diffusion.

Prior to the systematic experiments, H-Beta-75 was tested at 523 K, 2 MPa, and 1500 rpm by using different catalyst particle sizes. The results confirmed that the effect of internal diffusion on the reaction was negligible when using the catalyst particle fractions below 63 µm. Similarly, the influence of external diffusion was determined by varying the stirring rate. Due to the vigorous stirring (1500 rpm), the reaction was not limited by the external mass transfer. However, the plausible molecular and Knudsen diffusion effects in zeolite channels cannot be excluded.

The liquid reaction products were analyzed with a gas chromatograph (Agilent 6890N) equipped with a capillary column (DB-Petro 50 m × 0.2 mm × 0.5 µm) and a FI detector. Helium was used as a carrier gas. The following temperature program was applied: dwelling for 2 min at 323 K, heating 1.2 K/min to 393 K followed by heating 2 K/min to 473 K, and dwelling at 473 K for 20 min. Decalin yielded a wide variety of isomerization products (either isomers of decalin or isomers of ring-opening products), which were distinguished by the GC/MS technique. The GC/MS analysis was carried out in an HP 6890-5973 instrument. The same column and separation conditions as for the neat GC analysis were used. The composition of the gas-phase products was analyzed only for selected representative experiments after their completion.

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 and appears always as a part of the sample's name. Further characteristics of the zeolites can be found elsewhere [27].

The specific surface area of fresh and spent catalysts determined by N_2 adsorption is summarized as well in Table 1. All of the catalysts have very large specific surface areas (600–1200 m^2/g) calculated by the Dubinin method for the microporous materials and by the BET method for the mesoporous H-MCM-41. For the spent catalysts, a reduction of specific surface area was observed. Nevertheless, with the exception of H-Mordenite-20, the surface area of spent catalysts remains fairly high (over 400 m^2/g) after 9 h reaction 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 it is suggested by the corresponding decrease of the relative volume of micropores (Table 1), i.e., pores with diameters less than 2 nm [28]. The most prominent decrease of the surface area and the relative volume of micropores were observed for H-Mordenite-20 followed by H-Y-12.

The Brønsted and Lewis acidities of the studied catalysts, as determined by pyridine adsorption (FTIR), are presented in Table 2. All of the zeolites show a higher acidity than the mesoporous H-MCM-41. The highest concentration of Brønsted acid sites is found in H-Mordenite-20 despite that it has, apart from 12-membered rings, also 8-membered rings, which are virtually inaccessible for pyridine. The amount of BAS of H-Beta-25 is almost equal to that of H-Y-12, thus enabling a study of the zeolite-structure effect on ring opening. On the other hand, the amounts of BAS and LAS of H-Beta zeolites decrease with the increasing SiO_2/Al_2O_3 molar ratio, allowing an investigation of the effect of acid site concentrations on ring opening without any interference of pore-structure effects. Desorption of pyridine at different

Table 1
Specific surface area and relative volume of micropores of fresh and used catalysts, conditions; 523 K, 2 MPa, and 540 min

Catalyst	SiO_2/Al_2O_3, mol/mol	Specific surface area, m^2/g		Rel. volume of micropores[a], cm^3/g	
		Fresh	Used	Fresh	Used
H-Beta-25	25	807	461	0.052	0.027
H-Beta-75	75	664	566	0.038	0.037
H-Y-12	12	1218	496	0.051	0.019
H-Mordenite-20	20	605	87	0.012	0.002
H-MCM-41	35	1242[b]	770[b]	–	–

[a] Pores with diameter < 2 nm.
[b] BET.

Table 2
Brønsted and Lewis acidity of fresh catalysts

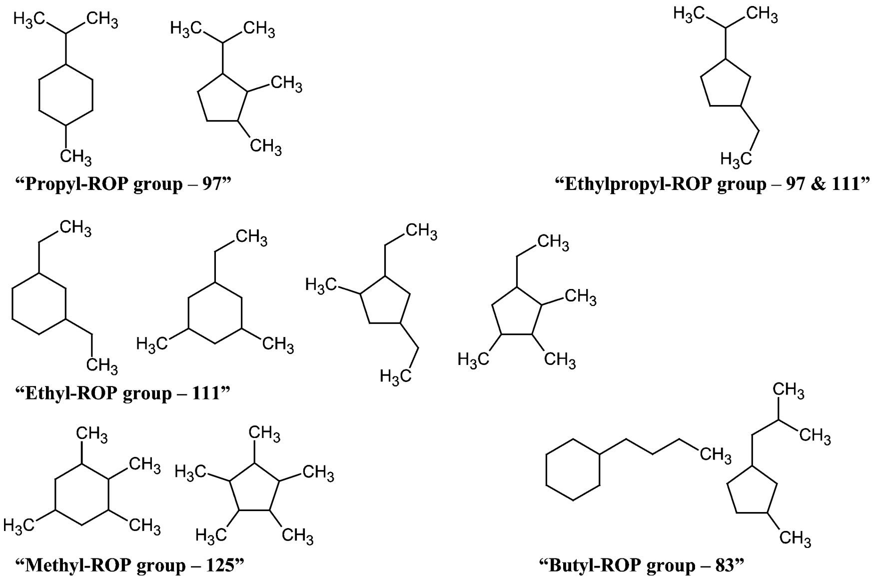
	Brønsted acid sites, μmol/g			Lewis acid sites, μmol/g		
Catalyst	523 K	623 K	723 K	523 K	623 K	723 K
H-Beta-25	269	207	120	162	128	113
H-Beta-75	147	135	114	39	29	16
H-Y-12	255	205	129	123	75	58
H-Mordenite-20	331	284	212	71	50	39
H-MCM-41	26	11	3	40	20	12

temperatures provides information about the strengths of the zeolite acid sites. Table 2 reveals that the majority of Brønsted acid sites being present in H-Beta-75 belongs to the strong BAS, which retain pyridine at 723 K. On the contrary, H-MCM-41 contains very few strong Brønsted acid sites. As the distribution and concentration of Brønsted sites in both H-Y-12 and H-Beta-25 are very similar, the two catalysts differ, from the acidity point of view, just in the concentration and relative strength distribution of the Lewis acid sites.

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 was called decalin. Any other C_{10} bicyclic structures were referred as decalin isomers or simply isomers (Iso); C_{10} monocyclic products, i.e., alkyl-substituted cyclopentanes and cyclohexanes, were denoted as ring-opening products (ROP). All products with a lower molecular weight than decalin were called cracking products (CP) and all products having more than 10 carbon atoms in the molecule and C_{10} aromatics were named heavy products (HP). Because of the high complexity of the reaction mixture, especially in the region of Iso and ROP elution from the GC column, not all of ROP and Iso compounds could be fully resolved. The problem was surmounted for overlapping peaks of ROP and Iso by determining the conversion dependency of the ratio of ROP/(ROP+Iso) for all such peaks by GC/MS analysis. The obtained ratio was used to calculate the concentration of ROP and Iso in the peaks. The response factors of MS were assumed to be the same for the overlapped ROP and Iso molecules.

However, for a more detailed analysis of the reaction system and elucidating the (individual) steps and intermediates involved in decalin conversion into ring-opening products, the basic grouping had to be refined. The detailed grouping was based on the GC/MS analysis, which provided data needed for structural characterization of products and thus enabled their classification into a particular product group. The ROP were divided into 5 ROP groups as follows: methyl-ROP (125), ethyl-ROP (111), propyl-ROP (97), ethylpropyl-ROP (97 and 111), and butyl-ROP (83). The number in parentheses denotes the dominant MS fragment, which results from a corresponding alkyl group loss from ROP having molecular weight equal to 140. Typical structures of all ROP groups are given in Fig. 1. The organization of Iso into groups


“Propyl-ROP group – 97”

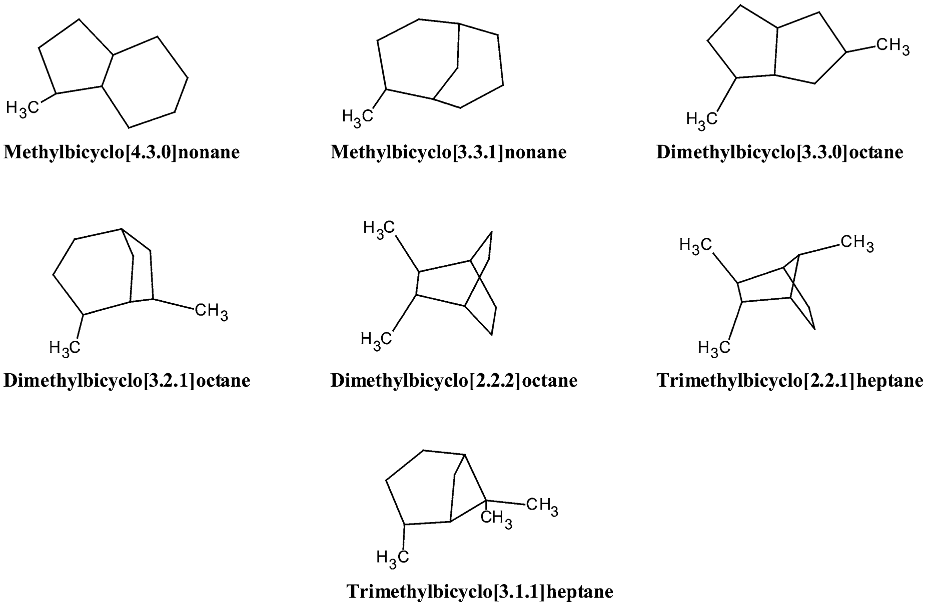
“Ethylpropyl-ROP group – 97 & 111”

“Ethyl-ROP group – 111”

“Methyl-ROP group – 125”

“Butyl-ROP group – 83”

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



Methylbicyclo[4.3.0]nonane **Methylbicyclo[3.3.1]nonane** **Dimethylbicyclo[3.3.0]octane**

Dimethylbicyclo[3.2.1]octane **Dimethylbicyclo[2.2.2]octane** **Trimethylbicyclo[2.2.1]heptane**

Trimethylbicyclo[3.1.1]heptane

Fig. 2. Typical isomer structures.

was even more complicated as there are only few spectra of those structures available in the standard GC/MS libraries. The fragmentation data from the literature [29] were taken into account together with the observed kinetic behavior of particular compounds in case of uncertainties. The following 6 groups were established: methylbicyclo-[4.3.0]nonanes, methylbicyclo[3.3.1]nonanes, dimethylbicyclo[3.3.0]octanes, dimethylbicyclo[3.2.1]octanes, ethyl-substituted bicyclooctanes, and trimethylbicycloheptanes. The last group consists of trimethylbicyclo[2.2.1]heptanes, trimethylbicyclo[3.1.1]heptanes, and dimethylbicyclo[2.2.2] octanes, as those could not be easily distinguished and were present in the lowest amounts from all the isomer groups. All products, which showed the characteristic loss of an ethyl group, i.e., strong mass fragment 109, were assigned to the group of ethylbicyclooctanes. Some representative structures of the Iso groups are shown in Fig. 2.

Major cracking products were identified as cyclic hydrocarbons C_5–C_9 and isobutane. A typical composition of CP for different temperatures is given in Table 3. No olefins and only traces of aromatics were found in the products. The main heavy products were methyl- and dimethyldecalins or their isomers. Their occurrence can be explained by a transalkylation reaction of ROP and CP with Iso and decalin. This is in agreement with the CP composition, where C_8 and C_9 cyclic hydrocarbons were present even though only traces of methane and ethane could be found in the gas phase. The most abundant hydrocarbon in the gas phase was isobutane. Furthermore, no C_9 bicyclic hydrocarbons were found among the products. This together with the absence of C_{11} monocyclic hydrocarbons excludes the possibility of C_9 monocyclic hydrocarbons being formed by ring opening of such C_9 bicyclic hydrocarbons.

Table 3
Molar composition of cracking products after 9 h over H-Beta-25 at various temperatures and 2 MPa

Hydrocarbon type	Temperature, K				
	513	523	533	543	553
C_3	0.06	0.10	0.12	0.20	0.25
C_4	0.68	1.05	1.28	2.21	2.81
C_5	0.20	0.37	0.51	1.05	1.35
C_6	1.16	1.75	2.32	3.93	4.77
C_7	1.08	1.64	2.33	4.04	4.87
C_8	0.58	1.00	1.45	2.87	3.23
C_9	0.17	0.34	0.55	1.19	1.27
Total	3.93	6.25	8.55	15.50	18.56
Naphthenics	2.94	4.60	6.42	11.46	13.46
Alkanes	0.97	1.62	2.08	3.93	4.97
Aromatics	0.02	0.03	0.05	0.12	0.14
Total	3.93	6.25	8.55	15.50	18.56
Conversion, mol%	57.77	68.64	74.52	84.25	85.87

3.3. *Initial activity of catalysts*

The total conversion of both bicyclo[4.4.0]decane isomers (*cis*- and *trans*-decalin) after 1 h was used as the measure for the initial activity comparison of the investigated catalysts. However, it should be noted that stereoisomerization of *cis*- to *trans*-decalin over proton-form zeolites occurs at the same temperature (Section 3.5.2). The initial activity decreases in the following order: H-Beta-25 > H-Y-12 > H-Beta-75 ≫ H-Mordenite-20 > H-MCM-41 (Table 4). For all catalysts except H-Mordenite-20, the initial activity follows the trend of increasing catalyst acidity, as reported in Table 2. This clearly indicates the importance of acid sites.

In fact, the mesoporous molecular sieve catalyst, H-MCM-41, has practically no activity. The concentration of Brønsted acid sites of H-MCM-41 is one order of magni-

Table 4
Initial molar conversions (after 60 min) at various temperatures and 2 MPa

	Temperature, K					
Catalyst	503	513	523	533	543	553
H-Beta-75	–	10.96	16.04	22.43	27.51	41.14
H-Beta-25	–	23.60	30.20	29.65	44.25	49.52
H-Y-12	17.73	19.83	23.71	29.10	29.66	–
H-Mordenite-20	0.16[a]	–	1.38	–	4.35[b]	–
H-MCM-41	–	–	–	–	–	0.38[c]

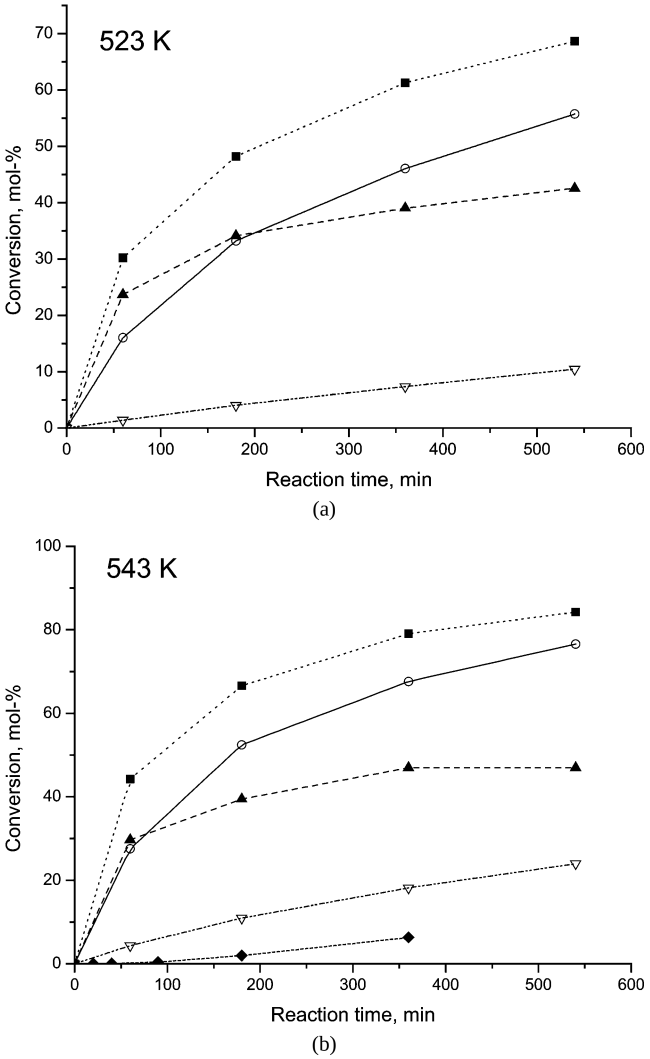
[a] At 498 K.
[b] At 548 K.
[c] At 573 K.

tude less than that for other catalysts and virtually no strong Brønsted acid sites are present. Comparison of H-MCM-41 and H-Beta-75 reveals that the concentration of Lewis acid sites and their strength distribution are almost identical for both catalysts. As their initial activities are very different, it can be concluded that it is the presence of Brønsted acid sites, which is crucial for ring-opening and isomerization activity of the catalysts (Table 2). Similarly, it might be expected if only Brønsted acidity determines the catalyst performance that H-Mordenite-20 exhibits the highest activity, as it has the highest concentration of Brønsted acid sites. Nevertheless, it shows the lowest activity among the investigated zeolite catalysts. The deviation from the pattern recognized for the remaining catalysts can most probably be explained by a rapid blockage of 12-membered ring pores by coke or adsorbed hydrocarbon molecules at the pore entrance, resulting in its very fast deactivation as discussed in more detail below.

An increase in reaction temperature resulted for the screened catalysts in a higher initial activity. It is noteworthy that even the increase of temperature to 573 K did not produce any significant increase in the activity of H-MCM-41. The reason is the extremely low concentration of Brønsted acid sites in H-MCM-41. In the case of H-Y-12 the obtained gain in activity with rising temperature is relatively lower than that of Beta zeolites. It is attributed to faster deactivation at higher temperatures already in the sample withdrawn after 1 h, as will be discussed.

3.4. Catalyst deactivation

During the reaction the catalyst activity was changing. The conversion achieved after 9 h decreases in the following order: H-Beta-25 > H-Beta-75 > H-Y-12 ≫ H-Mordenite-20 > H-MCM-41 (Fig. 3), which differs from the order of the initial activities. Higher conversions were obtained over H-Beta-75 than over H-Y-12 after 180 min of reaction, even though H-Y-12 exhibited a higher initial activity. The data displayed in Fig. 3 disclose that the conversion over H-Y-12 remains almost unchanged after 180 min. The conversion of decalin thus cannot be only assigned to the catalyst acidity, but it is dependent on the zeolite structure as well. For the same structure (Beta zeolite) the activity increases with the zeolite acidity (Fig. 3 and Table 2), as does the deactivation (Table 1).



(a)

(b)

Fig. 3. Decalin conversion over H-Beta-25 (■), H-Beta-75 (○), H-Y-12 (▲), H-Mordenite-20 (▽), and H-MCM-41 (◆) at [A] 523 K, [B] 543 K and 2 MPa. Data in [B] for H-MCM-41 are at 573 K.

However, the two other catalysts of approximately the same (H-Y-12) or even higher acidity (H-Mordenite) than H-Beta-25 exhibit a lower activity. It results from their faster deactivation, as revealed by a comparison of fresh and spent catalyst surface areas (Table 1). It is highly probable that for H-Mordenite-20 the coking takes place on the outer surface and at pore mouths, leading to a blockage of both 8- and 12-membered-ring channels by large hydrocarbon molecules and/or carbon deposits and resulting in a dramatic loss of its surface area (600–80 m^2/g). The deactivation of H-Y-12, which is witnessed at 543 K in the initial sample after 60 min, can be explained by the formation of deposits inside the cavities from larger molecules, which can be formed and remain trapped inside. This is in contrast to Beta zeolite with only a 3D channel system, which does not enable formation of larger intermediates inside the pore system. The phenomenon of initial deactivation of acidic faujasite zeolites has been discussed by several authors [19,30]. The deactivation has been ascribed to the formation of condensation products (dimers and trimers), which remained trapped inside the zeolite pores. The higher stability of Beta zeolites as compared to Y zeolites has been recently reported by Gopal and Smirniotis [31] for cyclopentane hydroconversion over bifunctional Pt/H-zeolites.

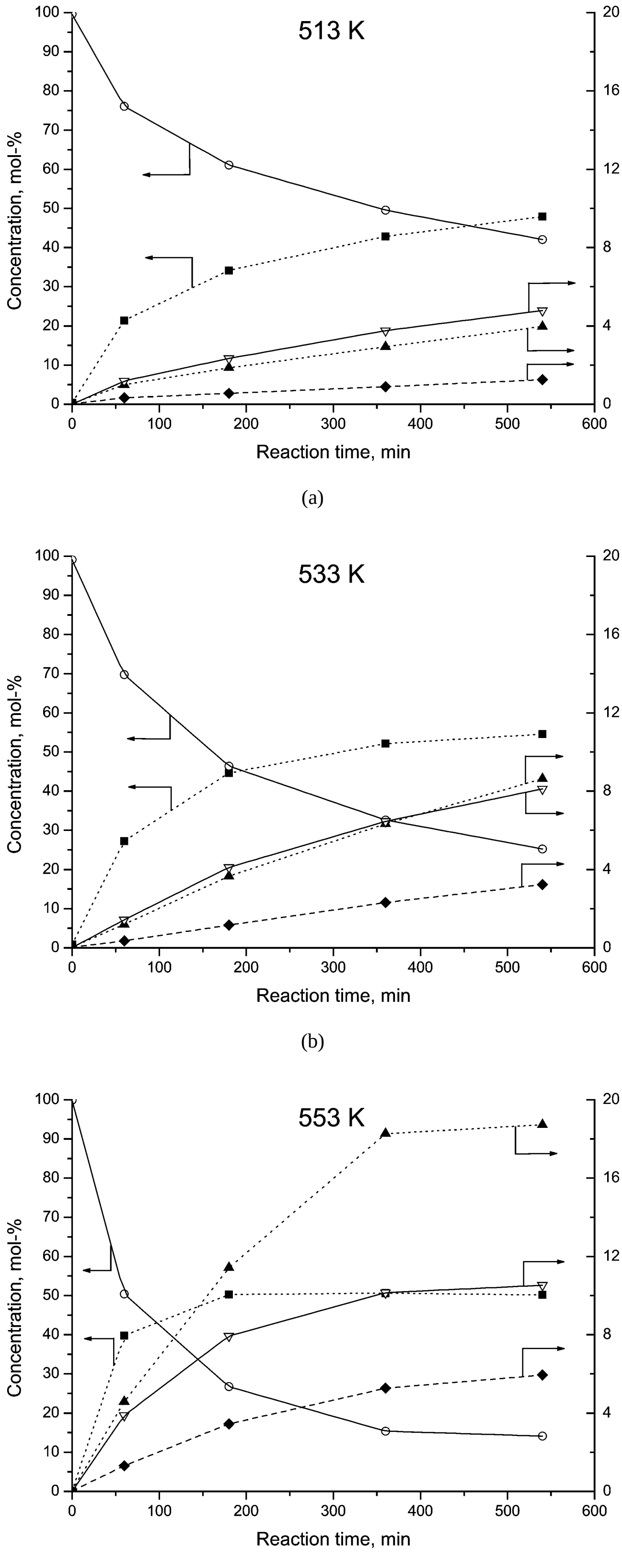
To confirm the hypothesis of initial deactivation of H-Y-12, GC/MS analysis of soluble deposits on spent catalysts was performed according to the procedure of Guisnet and Magnoux [32]. It revealed the presence of decalin dimers (compounds with molecular weights equal to 274). In fact these structures were the most abundant among the compounds present in the dissolved coke. The coke analysis thus, together with the surface area measurements and differences of the pore structures of the screened zeolites, supports the concept of rapid initial deactivation of highly acidic zeolites.

3.5. *Distribution of reaction products*

3.5.1. *General product distribution*

The product distribution as a function of the reaction time over the most active catalyst, H-Beta-25, is displayed in Figs. 4A–4C for three different reaction temperatures, 513, 533, and 553 K, respectively. It can be seen that the conversion (consumption of decalin) increases with the reaction temperature. Isomers are the primary products of decalin conversion and they are consumed by a consecutive reaction to produce ring-opening products. This is more clearly seen from the dependence of Iso and ROP on conversion, which will be discussed below. The ROP react easily further yielding cracking products. It is clear that increasing reaction temperature favors the conversion of ROP into CP. A simplified reaction network is given in Scheme 1. The amount of heavy products increases with reaction time and temperature. It is associated with the growing concentration of products, which can undergo transalkylation.

The differences in the product distribution as a function of the reaction temperature after 360 min are presented for H-Beta-25, H-Beta-75, H-Y-12, and H-Mordenite-20 in Fig. 5. The same trends in product distribution were observed in the time interval from 180 to 540 min. The data for all product groups indicate a dissimilarity of investigated Beta zeo-

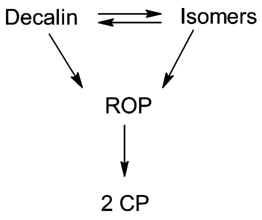


(a)

(b)

(c)

Fig. 4. Product distribution over H-Beta-25 at [A] 513 K, [B] 533 K, [C] 553 K and 2 MPa. Product groups: Decalin (○), Iso (■), ROP (▽), CP (▲), and HP (◆).

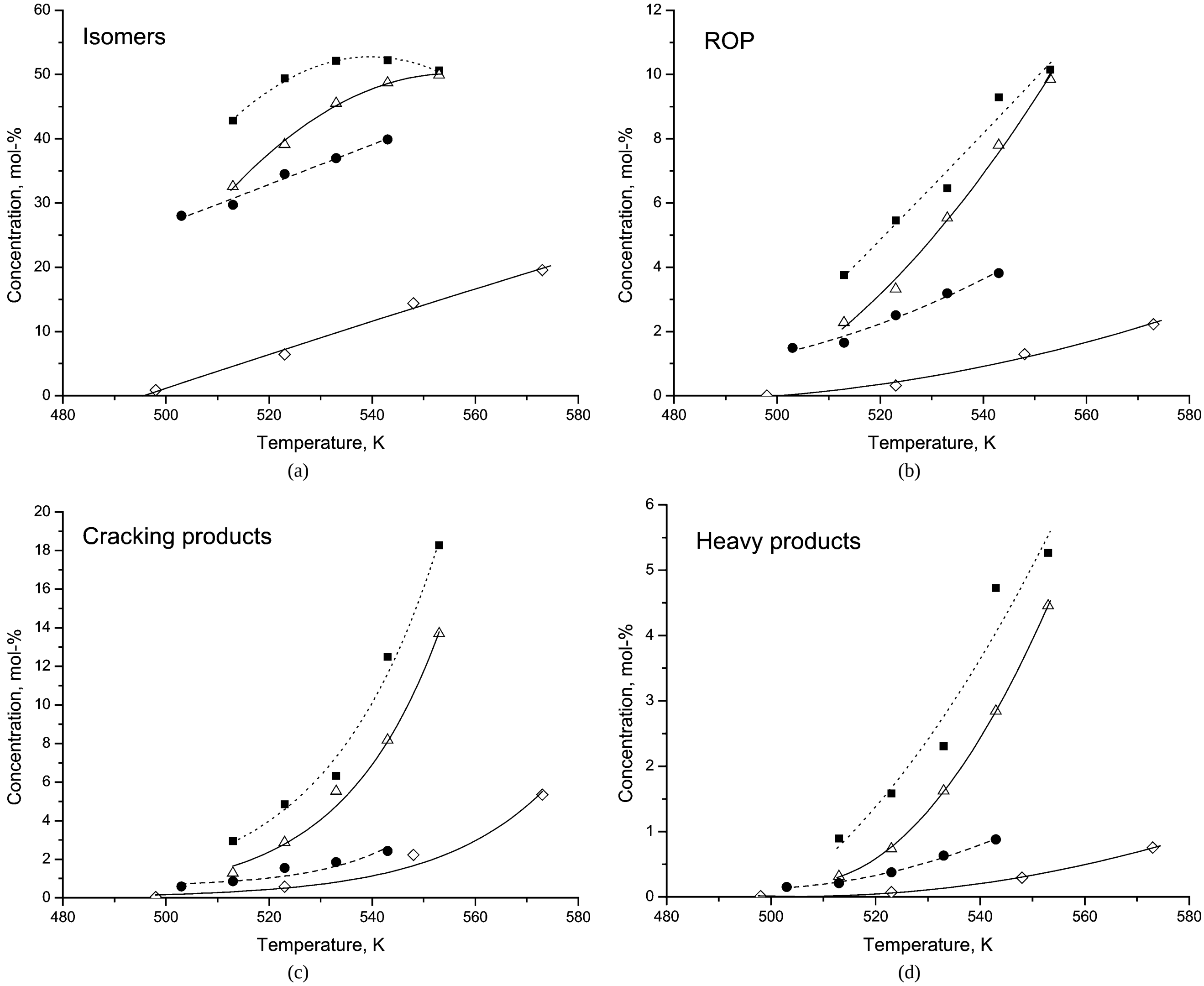


Scheme 1. Simplified reaction scheme.

lites on one hand and H-Y and H-Mordenite catalyst on the other hand. The difference could be misleading if the product distribution is not considered at the same conversion. Such comparison is presented in the sequel.

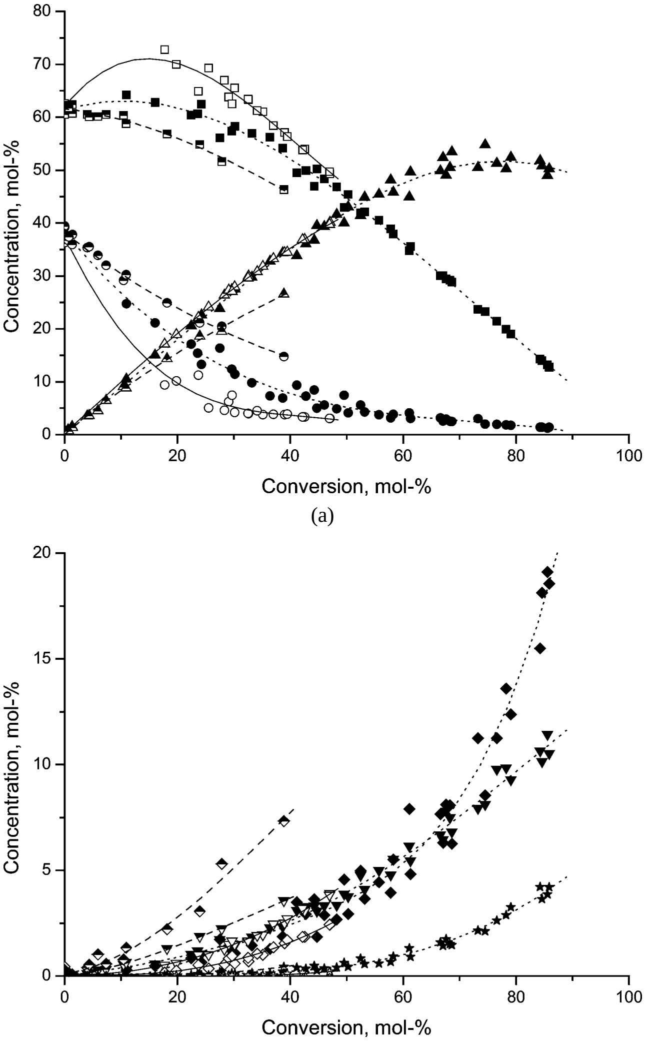
A low activity of H-Y and H-Mordenite over the temperature range investigated can be observed. However, the H-Y zeolite performance varies from that of H-Mordenite, as it exhibits a rather high isomerization activity. Nevertheless, the formed isomers are converted to ROP to a lesser extent than over Beta zeolites. While the concentration of isomers over H-Y at 543 K amounts to almost 80% of the Iso formed over H-Beta-25 under the same conditions, the concentration of ROP reaches only 45% of the ROP produced over H-Beta-25. This can be ascribed to the rapid deactivation of H-Y zeolite and its rather high initial activity, which hinders the consecutive ring-opening reaction. This explanation is further supported by the low extent of the next reaction step, cracking. The concentrations of the cracking products formed over H-Y zeolite represent just 20% of CP arising from H-Beta-25.

The maximum yield of isomers is achieved over the less acidic H-Beta-75 at higher temperatures than over H-Beta-25. This is not surprising, because the lower acidity and thus catalytic activity are compensated by the temperature increase. However, the extensive cracking over the highly acidic H-Beta-25 diminishes the yield of ROP, which is almost the same for both Beta zeolites at 553 K as is the yield



(a) (b) (c) (d)

Fig. 5. Temperature dependence of product concentration after 360 min over H-Beta-25 (■), H-Beta-75 (△), H-Y-12 (●), H-Mordenite-20 (◇). Concentration of isomers [A], ROP [B], cracking products [C], and heavy products [D].



(a)

(b)

Fig. 6. Concentration of reactants and main reaction product groups as a function of conversion for H-Beta-25 and H-Beta-75 (filled), H-Y-12 (open), and H-Mordenite-20 (half-filled). Reactants and product groups: [A] *trans*-decalin (■, □, ⬒), *cis*-decalin (●, ○, ◓), and isomers (▲, △, ◭), [B] ROP (▼, ▽, ⧩), CP (◆, ◇, ⬘), and HP (★, ☆, ⯪).

of isomers at this temperature. Nevertheless, the yields of the cracking and heavy products are lower over H-Beta-75 amounting to 75 and 85%, respectively, of the yields achieved over the H-Beta-25. This indicates that ring opening and cracking are the reaction steps most sensitive to catalyst acidity and temperature. In contrast to cracking and ring opening, the initial isomerization can be accomplished within the studied temperature range fairly easily and it is not very strongly dependent on the temperature (Fig. 5).

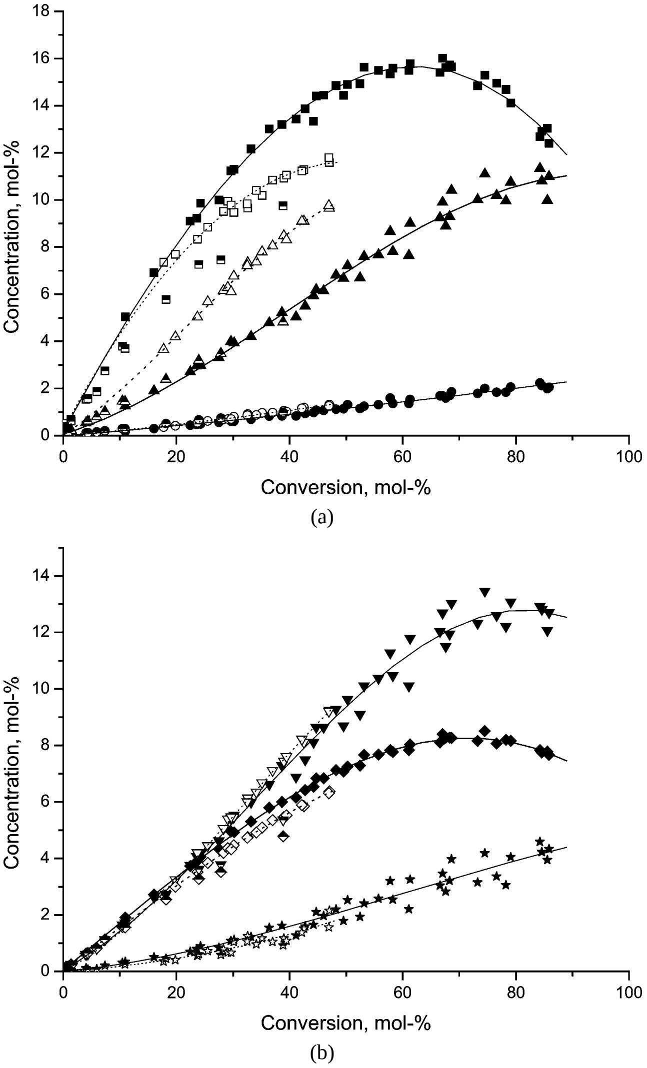
Fig. 6 summarizes the information obtained from all the experiments with zeolite catalysts in the studied reaction temperature range as a function of the conversion. An examination of Fig. 6 reveals that the product distribution over H-Y-12 and both H-Beta zeolites is not affected by their acidity, but depends mostly on the achieved conversion. A difference in the selectivity is, however, observed in the case of H-Mordenite-20. The cause of its low activity is the blockage of 12-membered ring channels by coke or adsorbed hydrocarbons at the pore mouth, leading to its fast deactivation. Nevertheless, relatively high amounts of cracking products were formed, as compared to the formation of ROP (Fig. 6B). It can be explained by the enhanced cracking activity of H-Mordenite-20 due to its high concentration of strong Brønsted acid sites, as compared to the other catalysts. In the case of H-MCM-41 only isomerization was observed, but virtually no ring-opening and cracking products were formed. This is in agreement with the presented reaction network scheme: as the H-MCM-41 solely possesses very mild acid sites and the achieved conversion is thus very low; just the initial reaction of decalin transformation, isomerization, takes place. Furthermore, it can be concluded that the differences observed in the product distribution at various temperatures are closely connected with the accomplished conversion as well, regardless of the temperature (Fig. 6).

3.5.2. *Stereoisomerization of decalin*

Despite the same product distribution among the major product groups (Iso, ROP, CP, and HP), the conversions of *cis*- and *trans*-decalin differ over the various catalyst structures, H-Y, H-Beta, and H-Mordenite (Fig. 6A). No difference is witnessed between the Beta zeolites despite their different acidities. As in the case of Iso and ROP, the experimental points follow the same trend for all temperatures over a particular catalyst. This indicates that the differences in the behavior of *cis*- and *trans*-decalin stem from the decalin stereoisomerization (*cis*- to *trans*-decalin isomerization) and not from the skeletal isomerization of decalin (isomerization of decalin to isomers).

The observed higher stereoisomerization activity of H-Y-12 compared to both investigated H-Beta zeolites is in contrast to the lower activity of H-Y-12 caused by its rapid initial deactivation (Figs. 3A, 3B, 7A, and 7B). Several authors [22,23] have reported the shape-selective behavior of H-Y zeolite in the stereoisomerization of decalin. The selective reaction was attributed to slightly smaller molecular dimensions and more flexible conformation of *cis*-decalin. The experiments with pure isomers also revealed a fast stereoisomerization of *cis*-decalin. The reverse reaction proceeded very slowly [22,23].

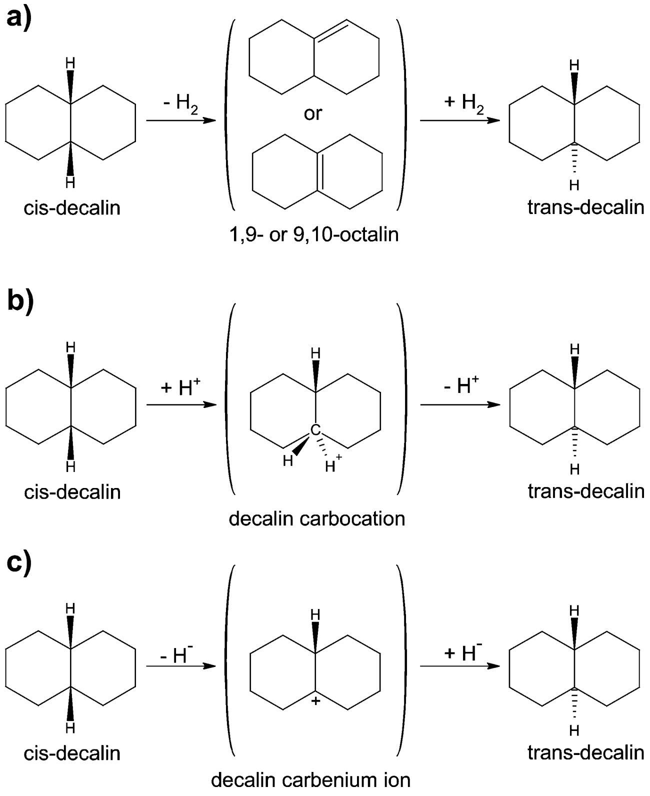
Lai and Song [33] studied the stereoisomerization of *cis*- and *trans*-decalin in more detail over proton-form and metal-modified zeolites. They found the isomerization over Pt- and Pd-modified zeolites to be more rapid than over proton-form zeolites. At the same time, the authors considered the same mechanism for the proton-form zeolites as the one proposed by Weitkamp [34] for metal-supported catalyst. It consists of the initial dehydrogenation of decalin to 1.9- or 9,10-octalin followed by subsequent hydrogenation yielding the other isomer (Scheme 2a). In the present case of the proton-form zeolites, it is more probable to assume that there is a protonation of tertiary carbon by Brønsted acid sites form-



(a)

(b)

Fig. 7. Concentration of isomers groups as a function of decalin conversion for H-Beta-25 and H-Beta-75 (filled), H-Y-12 (open), and H-Mordenite-20 (half-filled). Isomer groups: [A] Methylbicyclo[4.3.0]nonanes (■, □, ⬒), dimethylbicyclo[3.2.1]octanes (▲, △, ◭), and trimethylbicycloheptanes (●, ○, ◓), [B] dimethylbicyclo[3.3.0]octanes (▼, ▽, ⧩), methylbicyclo[3.3.1]nonanes (◆, ◇, ⬙), and ethyl-substituted bicyclooctanes (★, ☆, ⯪).



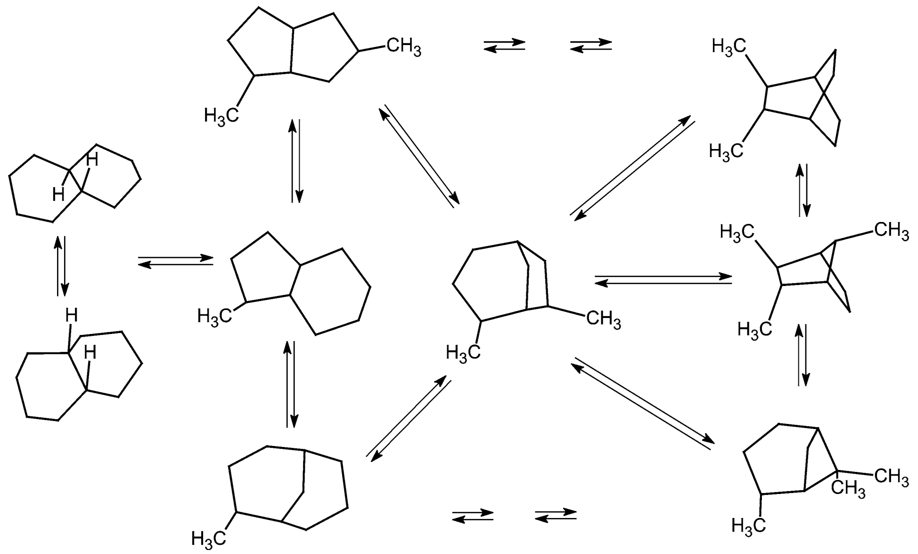
Scheme 2. Isomerization of *cis*-decalin to *trans*-decalin. (a) Dehydrogenation/hydrogenation mechanism [33], (b) protonation/deprotonation mechanism, (c) mechanism involving carbenium ion, for details on carbenium ion formation see text.

ing a pentacoordinated carbocation. This can in turn donate a proton to a framework oxygen atom and thus form the other isomer (Scheme 2b). Besides the proton exchange, the stereoisomerization of decalin can proceed via carbenium ions (Scheme 2c) formed on Brønsted acid sites by protolytic dehydrogenation [11–14,35] or on Lewis acid sites by hydride abstraction [12,35] followed by hydride addition. The reactions of saturated hydrocarbons in zeolites including the proton exchange have been reviewed recently by Ángyán et al. [36].

3.5.3. Skeletal isomerization of decalin

For a deeper understanding of decalin transformation into the desired ring-opening products knowledge of its isomerization is essential. It is well known that the six-membered hydrocarbon rings are the most stable, having the least strain in the molecule [37]. It has been shown for cyclohexane as well that a direct ring opening of six-membered hydrocarbon rings is unfavorable and the isomerization to methylcyclopentane is needed to facilitate the ring opening to acyclic hydrocarbons [4]. This agrees with the observations of the present study. Decalin conversion into ROP consists of several consecutive reaction steps, with the isomers being the primary and most abundant product group. Nevertheless, detailed GC/MS analysis revealed the complexity of the skeletal isomerization of decalin, comprising several parallel and consecutive reaction steps. The kinetic curves of all the isomer groups, as defined above, are collected in Fig. 7. It follows that there is no dependence of the overall isomer and ROP selectivities on the reaction temperature in the temperature range studied (Fig. 6). Thus again the data from all of the experiments are summarized in a single figure to elucidate the effect of different proton-form zeolites on skeletal isomerization and ring opening. The proposed reaction network based on the observed behavior (e.g., initial curve slopes) of the identified isomer structures, corresponding to the current knowledge of the reaction intermediates and their identification, is displayed in Scheme 3.

The reaction network scheme shows the initial ring contraction of decalin to methylbicyclo[4.3.0]nonanes followed by their isomerization to bridged bicyclononanes (methylbi-



Scheme 3. Proposed isomerization reaction network for decalin.

cyclo[3.3.1]nonane) or further ring contraction to dimethylbicyclo[3.3.0]octane. Those can yield by ring contraction or isomerization dimethylbicyclo[3.2.1]octanes, which can be further converted into trimethylbicycloheptanes structures (trimethylbicyclo[2.2.1]heptanes and trimethylbicyclo[3.1.1]heptanes) or dimethylbicyclo[2.2.2]octanes. Even though only methyl derivatives are noted here, the presence of ethyl or propyl substituents cannot be omitted. In fact, the ethyl-substituted isomers were identified based on the strong MS fragment 109, which is characteristic of the loss of an ethyl group from the parent isomer with a molecular weight of 138. Furthermore, as indicated by the reaction scheme, other intermediates may be possible as well.

Fig. 7 discloses some differences in the distribution of particular isomers groups for the different catalyst structures. This is interesting, especially, for H-Beta zeolites and H-Y-12, which showed the same dependency of the isomer concentration on the conversion (Fig. 6A). Nevertheless, clear variation of abundance of several isomers can be found. On the contrary, both H-Beta zeolites show identical trends despite their different acidic properties. The main deviation between H-Y-12 and both H-Beta zeolites lies in the concentration of methylbicyclononanes (methylbicyclo[4.3.0]nonanes and methylbicyclo[3.3.1]nonanes), which are less abundant over H-Y-12. Conversely, the Beta zeolites yield less dimethylbicyclooctanes, in particular dimethylbicyclo[3.2.1]octanes (Fig. 7A). Up to now it was not possible to determine unambiguously whether there is a link between the highest stereoisomerization activity of H-Y-12 and the formation of dimethylbicyclo[3.2.1]octanes. Similar differences were reported for the stereoisomerization of *cis*-decalin and were attributed to the shape-selective properties of Y zeolite [22,23]. Furthermore there are no indications that the variations are related either to the catalyst acidity, as there is no difference between H-Beta-25 and H-Beta-75, or to the reaction temperature, as the temperature range investigated was the same for H-Y-12 and both H-Beta zeolites.

3.5.4. Ring opening of decalin and isomers

The ring opening of naphthenes was studied extensively, from a mechanistic point of view, only on metal catalysts so far. As noted before, the ring opening of five-membered hydrocarbon rings is favored to the ring opening of six-membered hydrocarbon rings. McVicker et al. have demonstrated this by using a series of unsubstituted bicyclic hydrocarbons [6]. The conversion over 0.9% Ir/Al_2O_3 increased in the following order: bicyclo[4.4.0]decane $<$ bicyclo[4.3.0]nonane $<$ bicyclo[3.3.0]octane and conversions of 4.4, 68, and 81%, respectively, were achieved. Furthermore, it was shown for alkyl-substituted cyclopentanes that the rate of ring opening decreases with an increasing number of ring substituents, i.e., with a decreasing number of secondary–secondary C–C bonds [3,6].

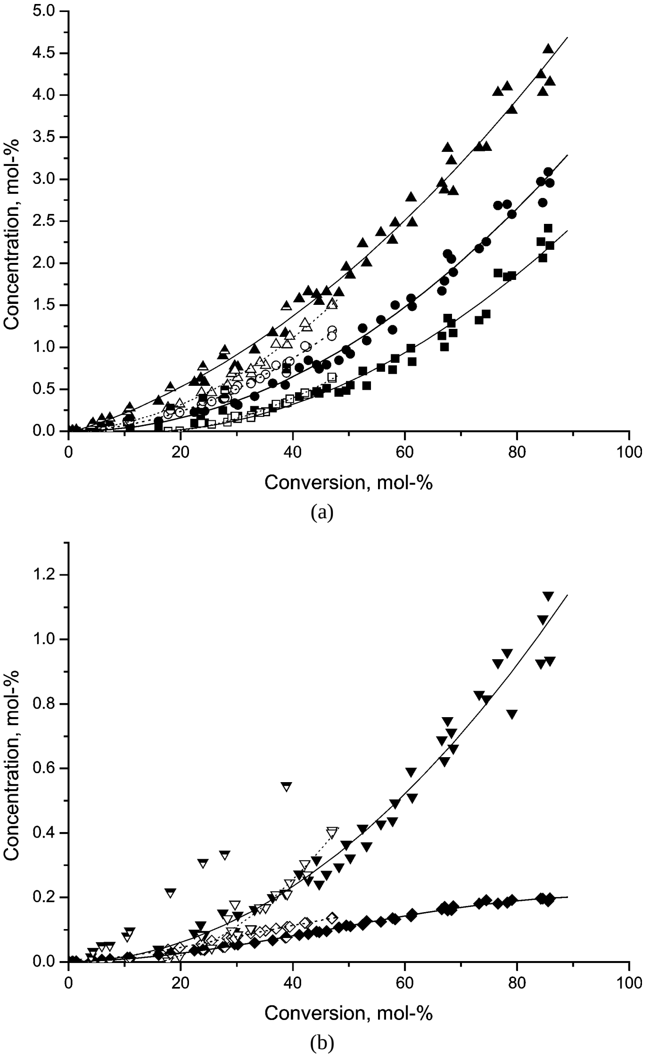
On the contrary, just a few reports exist for the ring opening of naphthenes on acidic sites of catalysts [21,23]. These do not, however, deal with the effects of the naphthene ring size and the degree of the ring alkyl substitution. Nevertheless, an analogy with cracking can be applied, assuming the adsorbed carbenium ions as a common reaction intermediate, as in fact ring opening is a specific kind of cracking. In addition to β-scission of carbenium ions, the protolytic cracking of isomers should be considered as well. Protolytic cracking of decalin can be omitted, since it has been shown that the majority of the ring-opening products originates from Iso.

In view of the fact that the isomerization of decalin leads to a complicated mixture of isomers, it is very difficult to interpret the origin of ring-opening products. In principle any of the isomers can yield a variety of ring-opening products—propyl-ROP, ethyl-ROP, ethylpropyl-ROP. Additionally, the ROP formed from isomers can undergo further isomerization. This is most probably the pathway of how methyl-ROP are formed, even though these products could as well be formed by ring opening of the "bridge" in dimethylbicyclo[2.2.2]octanes.

Strain in the hydrocarbon ring and number of alkyl substituents can be presumed to affect the ring opening of naphthenes. The least strain possesses the six-membered ring; five- and seven-membered have only a slightly higher strain in the molecule [37]. Thus this should not have a major effect on the stability of these hydrocarbons. On the other hand, smaller rings have a lot more strain and could thus be more easily opened than larger rings [37]. As a consequence, the more complex isomers (e.g., trimethylbicycloheptanes) will be more prone to ring opening than the less complex ones.

The number of tertiary carbon atoms, which form the most stable carbenium ions, may increase with the increasing number of alkyl substituents resulting hence in a higher probability of carbenium ion being formed from such isomers. A ROP is then formed by scission of the endocyclic C–C in the β-position from the atom bearing the charge. However, in a special case, quaternary carbon atoms, reducing the number of suitable positions for carbenium ion formation, can arise. From this viewpoint, the reactivity of dimethylbicyclooctanes should be higher than that of methylbicyclononanes.

A comparison of the ring-opening product distribution of the tested catalysts is based on all experiments in the temperature range studied (Fig. 8). Propyl-ROP is the most abundant group, followed by ethyl-ROP, methyl-ROP, and ethylpropyl-ROP. They all exhibit an increase with increasing conversion. Butyl-ROP (n-butylcyclohexane) is produced in small quantities only and its concentration is almost constant. Differences between H-Y-12 and the H-Beta zeolites were found, even though they were not as pronounced as in the case of isomers. No variation between the H-Beta zeolites was visible. Higher amounts of ethyl-ROP and lower amounts of propyl-ROP were formed over H-Y-12 as compared to H-Beta zeolites. This can be explained by the differences in isomer distribution over the catalysts investigated. It is less probable that the opening of the five-membered ring in dimethylbicyclo[3.2.1]octanes that are more abundant over H-Y-12 yields a propyl-ROP than it is in the case of methylbicyclo[4.3.0]nonanes, which are favored over Beta zeolites. The reason is that the five-membered ring in methylbicyclo[4.3.0]nonanes having a methyl substituent as a result of the ring contraction will primarily yield propyl-ROP as the main product assuming that a tertiary carbenium ion is the reactive intermediate and that an endocyclic bond in the slightly more strained five-membered ring is cleaved. The case of dimethylbicyclo[3.2.1]octane is more complex since the number of substituents on the five-membered ring can be in the range 0–2. Nevertheless, applying the same assumptions as in the case of methylbicyclo[4.3.0]nonanes, it can be shown that the main products will be ethyl-ROP, when 1 or 2 methyl groups substitute the five-membered ring. Methyl-ROP will be the primary product when both methyl groups are situated on the six-membered ring.



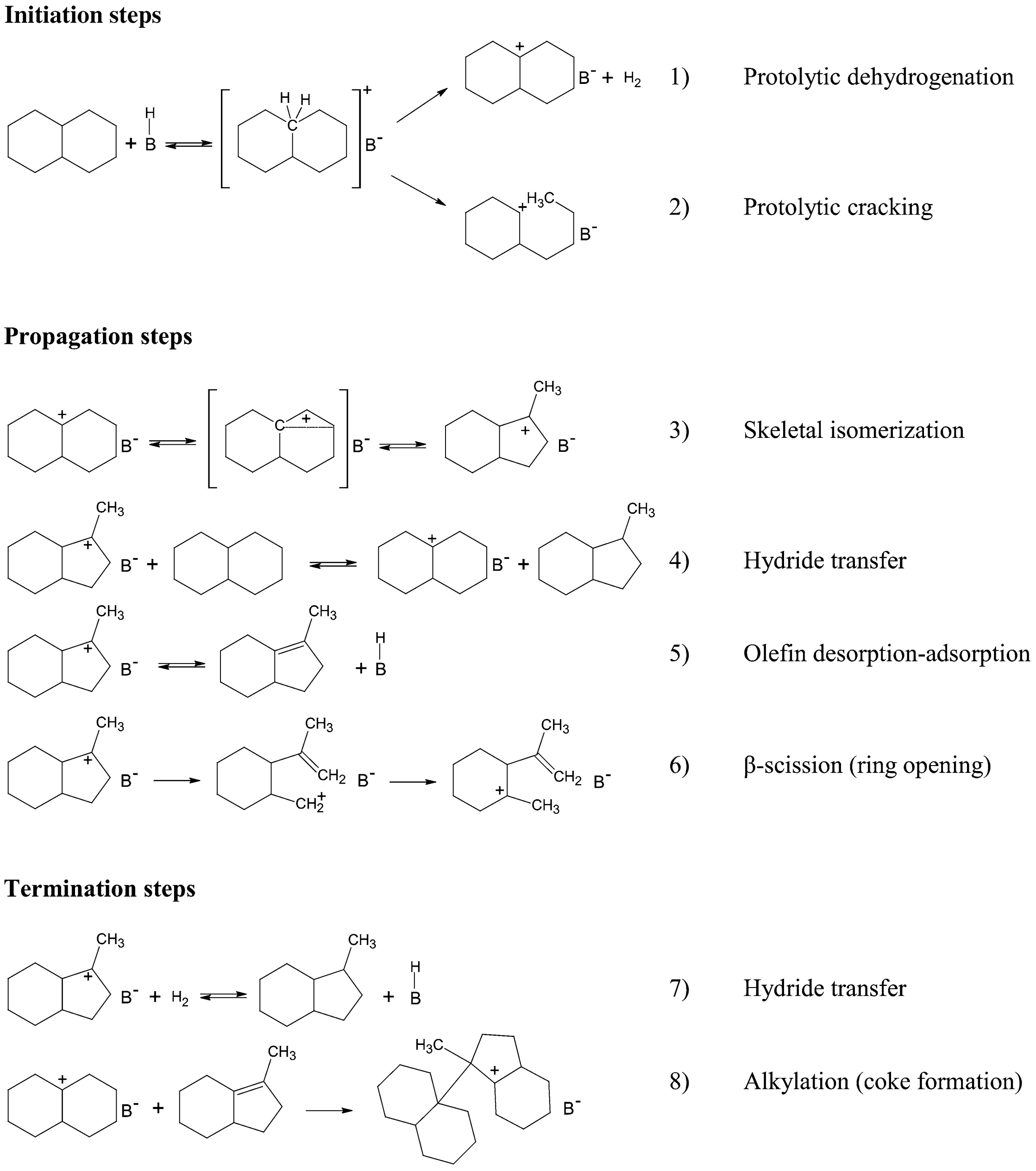
(a)

(b)

Fig. 8. Concentration of ROP groups as a function of decalin conversion for H-Beta-25 and H-Beta-75 (filled), H-Y-12 (open), and H-Mordenite-20 (half-filled). ROP groups: [A] Methyl-ROP (■, □, ⬒), ethyl-ROP (●, ○, ◓), and propyl-ROP (▲, △, ◭), [B] ethylpropyl-ROP (▼, ▽, ⧩), and butyl-ROP (◆, ◇, ⬘).

The maximum achieved yield of ring-opening products is 8 mol% over the proton-form zeolites. It was indicated in the literature [18] that the yield was higher when metal-modified zeolites were used. Ring-opening yields of 15–25 wt% were obtained in the ring opening of tetralin. The results confirming the enhancement of ring-opening selectivity due to the metal modification of zeolites along with detailed analysis of selectivity, which is lacking in the literature, will be reported in a separate paper.

A mechanism for decalin isomerization and ring opening (Scheme 4) can be proposed applying the cracking and isomerization pathways considered in the literature [11–14] in combination with the obtained product distribution. On solely acidic forms of zeolites the reaction is initiated by an attack of a Brønsted acid site on a carbon–carbon bond of



Scheme 4. Proposed mechanism for isomerization and ring opening of decalin.

decalin forming a carbonium ion [21]. This in turn yields a dinaphthene carbenium ion due to protolytic dehydrogenation (**1**) or an alkylnaphthene carbenium ion as a result of protolytic cracking (**2**). Since isomers are formed almost exclusively at the beginning of the reaction, it can be assumed that the protolytic dehydrogenation (**1**) is the prevailing initiation step. Either of the formed carbenium ions can undergo skeletal isomerization, which proceeds via the corner-protonated cyclopropane ring (**3**) [11], or hydride transfer from decalin to the adsorbed carbenium ion resulting in formation of decalin carbenium ions and desorption of the saturated product (**4**). Furthermore, the dinaphthene carbenium ion can undergo β-scission leading to an alkenylnaphtene carbenium ion (**6**). When the alkenylnaphtene carbenium ion is saturated, ring-opening product is obtained. This saturation includes hydride transfer on the charged carbon atom (**4**) and olefin adsorption on a Brønsted acid site (**5**) followed by another hydride transfer. Hydride transfer plays a vital role in the reaction mechanism. In order to obtain saturated products, as is the case here, formation of carbenium ions with relatively long lifetimes is needed to enable the hydride transfer reaction rather than the desorption of an olefin, which is governed by the olefin adsorption–desorption equilibrium (**5**) [38]. The average lifetime of adsorbed carbenium ions is longer on stronger acid sites, thus increasing the probability of bimolecular reactions, such as hydride transfer [14]. Hydride transfer is responsible for termination of the reaction cycle as well. Two alternatives can be considered: reaction of molecular hydrogen with carbenium ion (**7**) and hydride transfer from coke precursors. In the former alternative, hydride is donated by hydrogen to produce a naphthene from a corresponding carbenium ion. The resulting proton regenerates the original Brønsted acid site [13]. In the latter one, a hydride is supplied from coke precursors, formed by alkylation reactions (**8**), causing their aromatization [38]. The suggested coke precursor originating from the alkylation reaction (**8**) has the same molecular weight as the most hydrocarbons detected in the dissolved coke (see above). The alkenylnaphthene can be involved after protonation (adsorption) in another β-scission, competing with hydride transfer, which leads to formation of cracking products. The probability of this event increases with higher reaction temperature. In a special case, the alkenylcarbenium ion can internally react with the double bond in the alkyl chain to form a dinaphthene carbenium ion.

3.5.5. *Cracking products*

The concentration of cracking products increases with increasing temperature (Fig. 5C) and conversion (Fig. 6B). The detailed composition of cracking products at various temperatures is shown for H-Beta-25 in Table 3. Two kinds of cracking products can be distinguished, naphthenic and aliphatic hydrocarbons. Naphthenic hydrocarbons are formed by dealkylation of ring-opening products and the main products are methylcyclopentane, cyclohexane, dimethylcyclopentanes and methylcyclohexane (Table 3). Isobutane is the most abundant aliphatic hydrocarbon, which suggests that the entire C_4 chain is eliminated after ring opening. The cleavage is accompanied by the formation of cyclohexane, which readily undergoes isomerization to methylcyclopentane, the most abundant naphthenic hydrocarbon. The ratio between naphthenic and aliphatic hydrocarbons is constant regardless of the temperature. Moreover, the relative composition of cracking products (C_3–C_9) does not vary with the temperature as well (Table 3).

The same cracking products were obtained over all tested catalysts (Table 5), but the relative composition of CP depended on the catalyst used. Aliphatic hydrocarbons were more abundant than naphthenic hydrocarbons over H-Mordenite-20, which suggests that the CP formed from ROP undergo further cracking. It can be attributed to the strength of the Brønsted acid sites, as H-Mordenite-20 has the highest concentration of strong Brønsted acid sites (Table 2). Naphthenic hydrocarbons are the predominant CP over H-Beta and H-Y zeolites.

4. Conclusions

The activity of H-Beta-25, H-Beta-75, H-Y-12, H-Mordenite-20, and H-MCM-41 has been investigated in ring opening of decalin at 498–573 K in the presence of hydrogen. The ring opening of decalin has been found to proceed via several intermediates including different skeletal isomers of decalin. The isomer intermediates as well as the different types of ring-opening products have been identified and a reaction network for the skeletal isomerization of decalin is proposed. The major findings can be summarized as follows.

In order to achieve the formation of ring-opening products from decalin, its skeletal isomerization is needed prior to the ring opening. The presence of Brønsted acid sites is essential for the accomplishment of both isomerization and ring opening. The concentration of Brønsted acid sites is crucial for the catalyst activity; a higher Brønsted acidity results in a higher initial activity. The catalyst activity increases with the increasing reaction temperature as well.

Furthermore, the acidity together with the pore structure influences catalyst deactivation. Due to the high concentration of strong Brønsted acid sites, H-Mordenite undergoes a very rapid deactivation. H-Y-12 is found to deactivate more rapidly than H-Beta-25 despite the almost equal acidity. The difference is explained by the presence of large cavities in H-Y zeolite, which enable the formation of large organic molecules blocking the pores.

Methylbicyclo[4.3.0]nonanes, dimethylbicyclo[3.2.1]octanes, and dimethylbicyclo[3.3.0]octanes formed by decalin skeletal isomerization are the most abundant isomers, which are converted into ring-opening products. The main ring-opening products are propyl-ROP. Cracking, yielding mainly C_6-saturated naphthenic hydrocarbons and isobutane, proceeds simultaneously with ring opening and isomerization.

Dimethylbicyclooctanes are more abundant over H-Y than over H-Beta zeolites. On the contrary, more methylbicyclononanes are formed over Beta zeolites. The different isomer product distribution is reflected in the ROP distribution; relatively more ethyl-ROP and less propyl-ROP are observed over H-Y zeolites. The differences in skeletal isomerization and consequently in ring opening may be attributed to shape-selective properties of H-Y zeolites, as in the case of stereoisomerization of *cis*-decalin.

Table 5
Molar composition of cracking products after 9 h at 523 K and 2 MPa

Hydrocarbon type	Catalyst			
	H-Beta-25	H-Beta-75	H-Y-12	H-Mordenite-20
C_3	0.10	0.09	0.05	0.11
C_4	1.05	1.08	0.46	0.26
C_5	0.37	0.22	0.10	0.07
C_6	1.75	1.61	0.71	0.21
C_7	1.64	0.77	0.25	0.07
C_8	1.00	0.53	0.25	0.06
C_9	0.34	0.15	0.03	0.00
Total	6.25	4.44	1.85	0.78
Naphthenics	4.60	3.01	1.21	0.34
Alkanes	1.62	1.41	0.64	0.44
Aromatics	0.03	0.02	0.00	0.00
Total	6.25	4.44	1.85	0.78
Conversion, mol%	68.64	55.72	42.55	10.45

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