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Ring opening of decalin and tetralin on HY and Pt/HY zeolite catalysts

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Abstract

The removal of polynuclear aromatics from diesel fuel in response to increasingly stringent environmental legislation has stimulated intense research. In addition to the hydrogenation reaction that saturates aromatics, an interesting possibility is the opening of naphthenic rings derived from the saturation of aromatics to produce molecules of higher cetane numbers. In this contribution, we have investigated a series of HY and Pt/HY catalysts of varying acidity densities. Under the conditions of this study, mainly ring-contraction and one-ring opening reactions take place over these catalysts. Although the products from these reactions do not have cetane numbers significantly higher than those of the saturated aromatics, they can be important intermediates to high cetane number compounds, such as normal paraffins and some *iso*-paraffins. The results of this investigation show that HY zeolites can be effective catalysts for the ring contraction and one-ring opening of decalin if their acidity density is adjusted to an intermediate optimum, that is, high enough to achieve conversion, but not too high that would result in fast deactivation. The low *cis*-to-*trans* ratios obtained in the products are due both to the *cis*-to-*trans* isomerization, but more importantly, to a much higher reactivity of *cis*-decalin than *trans*-decalin. Also, *cis*-decalin converts much more selectively to ring-opening products than *trans*-decalin, which mainly converts to cracking products. The production of ring-contraction and ring-opening products from tetralin is greatly enhanced in the presence of Pt due to hydrogenation of tetralin to decalin. In the presence of hydrogen Pt/HY catalysts as well as physical mixtures of HY and Pt are much more effective than HY catalysts.

Keywords: Ring opening; Ring contraction; Cracking; Decalin; Tetralin; Aromatics; Diesel; Pt; HY zeolite

1. Introduction

Removal of polynuclear aromatics from diesel fuel (e.g., anthracene, naphthalene, tetralin) has become a focus of intense research due to the stringent environmental legislation associate with clean fuels [1–3]. In addition to their negative environmental impact, polynuclear aromatics decrease the cetane number and diminish the overall quality of the diesel. Two methods are currently being used to improve diesel quality by removal of polynuclear aromatics, ASAT (aromatic saturation) and hydrocracking, but both of them have some limitations. While ASAT preserves the diesel range molecular size, it cannot yield the high cetane numbers that will be required in the near future. Similarly, hydrocracking can produce compounds of higher cetane number, but it excessively reduces the molecular weight and produces lower yields in the diesel range. An interesting alternative that has been recently proposed is a combination of deep hydrogenation and selective ring opening (SRO) of naphthenic rings to alkanes [4]. Contrary to unselective cracking, ring opening could result in a high cetane product without the loss of reactant molecular weight. As illustrated in Scheme 1 for some relevant C10 compounds, the cetane number greatly increases when a molecule such as decalin with two naphthenic rings is converted into a paraffin. However, it must be noted that both the ring contraction and the one-ring-opening reactions that have been investigated in this work are only intermediate steps in this task. Neither ring con-

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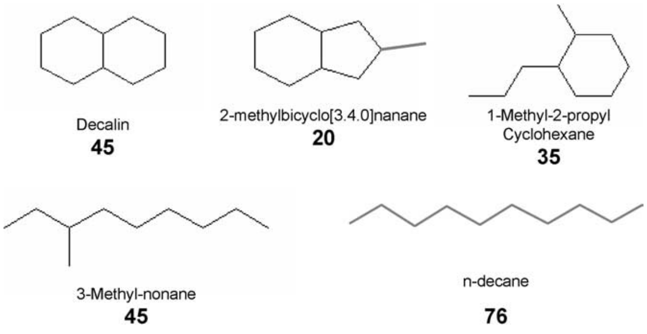


Scheme 1. Cetane numbers of decalin and some relevant products.

traction (RC) nor one-ring opening (RO) alone result in an improvement in cetane number. However, these reactions might play an essential role in generating the intermediate one-ring or C5-ring compounds that can be further converted to high cetane number compounds, such as normal paraffins and some *iso*-paraffins. This is an important point to emphasize because it may have been ignored in many of the previous investigations dealing with ring opening of decalin.

Although opening of a ring can be accomplished on either acid or metal catalysts, the combination of the two functions is much more effective than each of them alone. The opening of small ring cycloparaffins on solid acid catalysts has been studied for many years [5]. It is widely accepted that molecules with three- and four-member rings have a significant ring strain and, consequently, are more easily opened than the larger rings. As a result, cyclopropane and cyclobutane can be ring-opened at much lower temperatures than molecules such as cyclopentane and cyclohexane [6]. It has been proposed [3] that on acidic zeolites, the activation of six-member rings can occur on Brønsted sites via an initiation step described as a protolytic cracking (PC); subsequent steps follow the typical carbenium ion reactions, such as ring contraction (RC), β-scission cracking, and alkylation. Alternatively, formation of olefinic intermediates via H transfer could produce the carbenium ion without involvement of a PC step [7].

The majority of the ring-opening investigations found in the literature refer to single-ring molecules. On the other hand, while two-fused-ring compounds, such as decalin (decahydronaphthalene), tetralin (tetrahydronaphthalene), and naphthalene are much more relevant to LCO upgrading, detailed studies with these feedstocks are far less common. Only recently, a few interesting studies have attempted to gain insight on the complex mechanisms responsible for the different reactions undergone by two-fused-ring compounds. For example, Corma et al. [3] have studied the conversion of decalin and tetralin over proton-form zeolites of different pore sizes. They emphasize the role of the pore size and zeolite topology in determining the product distribution. Zeolites with large pores such as HY seem to be the most appropriate for selective ring opening. In the discussion of the possible mechanism of decalin conversion, they propose that the decalin activation starts with the opening of the ring via PC. In this scheme, the products of ring-opening would be primary while the products of ring-contraction isomerization would be secondary. By contrast, in a more recent investigation, Kubicka et al. [8] did not observe direct ring opening of decalin and proposed that RO is a secondary reaction, which is preceded by a step of a skeletal isomerization, ring contraction. The authors argue against the PC of decalin as an initiation step since the RO products seem to originate only from the RC products, such as alkyl bicyclononanes (indanes) and bicyclooctanes, which acted as intermediates. The evolution of RC and RO products as a function of conversion had nonzero and zero derivative at the zero conversion limit, respectively. This contrasting behavior strongly supports the notion that RC products are primary while RO products are secondary and are only detected after the concentration of RC products becomes sizeable. The reaction conditions of the two studies were significantly different; Corma et al. [3] worked in a flow reactor at atmospheric pressure (0.1 MPa), high temperatures (723 K), and with no added hydrogen; by contrast, Kubicka et al. [8] operated in a batch reactor, at higher pressures (2 MPa), lower temperatures (473–573 K), and at very low H_2/feed ratios (1/13).

The use of metals supported on acidic zeolites for ring opening of six-member ring naphthenics has attracted attention in recent years [9–11]. McVicker et al. [4] have shown that while alkylcyclopentanes can be readily ring-opened by low-temperature hydrogenolysis over noble metals such as Ir, the corresponding ring opening of alkylcyclohexanes is almost a hundred times slower. They have proposed that the addition of an acidity function provides the catalyst the necessary ring-contraction activity to allow selective conversion of six-membered-ring naphthenes. This result is in good agreement with previous observations that, on metals as well as on acid catalysts, a five-member ring opens much faster than a six-member ring [12]. Working on NiW/HY catalysts, Kustov et al. [13] found an interesting difference regarding the need for the acidic function in ring opening. They determined that acidity was essential for multiring compounds, such as decalin, but not for the single-ring cyclohexane, which can be opened on monofunctional metal catalysts. Arribas and Martinez [9] studied the combination of hydrogenation and ring opening of tetralin and 1-methylnaphthalene over Pt catalysts supported on various supports. Their results, obtained at a H_2/feed ratio of 30/1, showed that zeolite supports resulted in concentrations of RO products higher than other supports. Among the zeolites, those with large-pore sizes (USY, beta, mordenite) produced higher RO yields than zeolites with medium pore sizes. The degree of easiness of undocking the reactant molecules from the pores was considered as the key parameter that determines RO selectivity.

It is well known that on proton-form zeolites the ring opening of decalin is much faster than that of tetralin [3]. In a practical application, it is conceivable that aromatics such as tetralin or naphthalene would first undergo hydrogenation and subsequently the fully saturated decalin would be the reactive compound for the production of ring-opening products. Therefore, in the present contribution, the reactions of decalin and tetralin were investigated in a fixed-bed flow reactor at 2 MPa and 533 and 600 K, respectively, in the presence of excess hydrogen. We have selected the conditions that one would typically expect if the ring opening is conducted in combination with hydrogenation. These conditions are similar to those previously used by Arribas and Martinez [9] but differ significantly from those used by Corma et al. [3] and Kubicka et al. [8]. To systematically study the acid and metal functions, we have prepared a series of HY zeolites with varying degrees of ion exchange to vary the acid site concentration and on Pt-containing HY zeolite catalysts.

Decalin has two configurational isomers, *cis* and *trans*. Between the two isomers, *trans*-decalin is more stable because it has no axial substituents. *cis*-Decalin is conformationally more mobile than *trans*, but it is less stable because it has one axial substituent in each ring. From the hydrogenation of naphthalene and tetralin a mixture of *cis*- and *trans*-decalin is obtained. Depending on the catalyst and the reaction conditions, the *trans*/*cis* ratio may widely vary. Not only different catalysts have different selectivities toward *trans*- or *cis*-decalin, but also the *cis*-to-*trans* isomerization may affect the resulting *trans*/*cis* ratio [14,15]. A distinctive aspect of the present study is that we have paid special attention to the differences in reactivity for the two decalin isomers and conducted measurements with isomerically pure feeds. If, as we propose here, *cis* and *trans* have on HY catalysts a very different reactivity toward ring opening, a product optimization could be expected if one can maximize the concentration of the isomer that is most reactive toward ring opening. This contribution also includes a set of experiments that has not been done before in the study of tetralin conversion. These experiments compare the product distribution of different physical mixtures and segregated beds of individual Pt and HY catalysts to that of single bed Pt/HY and HY catalysts.

2. Experimental

2.1. Catalyst preparation

Three HY zeolite catalysts with varying acidity density were prepared by ion exchange of a NaY zeolite (Y54 from UOP, Si/Al = 5.3). In this procedure, 100 g of NaY was added into an aqueous solution containing 120.5 g ammonium chloride dissolved in a liter of deionized water. This suspension was refluxed and stirred with a magnetic plate for 2 h. The solid was then filtered and washed with deionized water; this solid with one ion exchange is identified as HY1. The HY2 and HY3 samples were prepared in a similar fashion, but with 2 and 4 sequential ion-exchange steps, respectively. After each ion-exchange step, the samples were filtered and washed. In the final step, each samples was further washed with deionized water until it was chloride free. It was finally dried in air at 383 K and kept in a desiccator. Prior to the activity measurements, the samples were calcined in flow of dry air at 823 K for 2 h.

In addition to the proton-form zeolites, a Pt-containing catalyst was prepared using HY3 as a support. The Pt/HY3 catalyst was prepared by incipient wetness impregnation (IWI) of the HY3 zeolite with hexacloroplatinic acid (Acros) of appropriate concentration to obtain a metal loading of 1.0 wt% Pt. After impregnation, the sample was dried at 383 K overnight and calcined at 573 K in oxygen flow for 3 h at a heating rate of 0.5 K/min. Prior to each activity measurement, the sample was reduced in situ. A 1% Pt/SiO_2 catalyst was used as a reference for monofunctional metallic Pt. This catalyst was prepared by incipient wetness impregnation of SiO_2 (Grace, grade 923, surface area 450 m^2/g) with a solution of hexachloroplatinic acid. After impregnation, the sample was dried in oven and calcined in a flow of air at 573 K for 3 h.

2.2. Catalyst characterization

2.2.1. Temperature-programmed desorption (TPD) of adsorbed ammonia

The acidity densities of the three zeolites HY1, HY2, and HY3 as well as the Pt/HY3 catalyst were determined by TPD of adsorbed ammonia. The test was conducted in a $\frac{1}{4}$-inch quartz tube reactor containing 50 mg of catalyst that was pretreated at 773 K for 1 h in He flow. Then, the sample was cooled down in He flow to room temperature, at which point, 2% NH_3/He was passed over the sample in an amount that greatly exceeds the total number of acid sites. To remove the excess and weakly adsorbed ammonia, the sample was purged in He flow at room temperature for 2 h. Subsequently, the sample was linearly heated to 973 K at a heating rate of 10 K/min while the evolution of ammonia was monitored in a thermal conductivity detector. After each TPD, the amount of ammonia adsorbed was determined by a calibration curve obtained by varying volumes of 2% ammonia in He.

2.2.2. FTIR of adsorbed pyridine

Infrared spectroscopic measurements of adsorbed pyridine (Py-IR) were recorded on a Bruker Equinox 55 spectrometer. Self-supported wafers of 75-mg samples with a diameter of 2.5 cm were placed in a cell with CaF_2 windows. Before pyridine adsorption, the sample was pretreated in He at 773 K for 2 h. After the pretreatment, the sample was cooled to a desired temperature (423 K) and a blank spectrum was taken. Subsequently, the sample was exposed to pyridine vapors for 2 h in order to saturate all the acid sites. Then, He was passed through the cell for 12 h to purge the excess of pyridine out from the cell. Four spectra were obtained for each sample at 423 K, first of the saturated sample, and then after outgassing at 523, 623, and 673 K. The absorption band appearing at 1545 cm^{-1} was assigned to the pyridinium ion formed on Brønsted acid sites, while the band at 1455 cm^{-1} was assigned to pyridine coordinated to Lewis acid sites. The density of both types of acid sites was quantified by integrating the corresponding absorption bands and using the molar extinction coefficients obtained by Emeis [16].

2.2.3. *Extended X-ray adsorption fine structure (EXAFS)*

The Pt L_{III} edge spectra (11564 eV) for fresh Pt/HY3 catalyst was measured at line X-11B, the National Synchrotron Light Source (running at dedicated mode of 2.81 GeV and 100–250 mA) at Brookhaven National Laboratory, Upton, NY. Energy was calibrated using an internal platinum foil standard. The measurements were conducted in a stainless-steel sample cell that allowed in situ pretreatments at temperature ranging from liquid nitrogen to 773 K. Prior to measurement, the fresh catalyst was reduced in situ at 673 K (heating rate of 10 K/min) for 30 min in flowing hydrogen. After the reduction step, the sample was cooled down in flowing hydrogen. The EXAFS spectra were recorded at liquid nitrogen temperatures under hydrogen flow. The average spectrum from 6 scans was used to analyze the sample.

For the data analysis, the preedge background was subtracted by using power series curves; the postedge background was then removed using a cubic spline routine; the spectra were normalized by dividing by the height of the adsorption edge; to avoid overemphasizing the low-energy region, the data were k^3-weighted. The k-space range used for the analysis was 2–16 $Å^{-1}$. To determine structural parameters, i.e., nearest neighbor distances and coordination numbers, curve fitting of the k-space EXAFS function and R-space Fourier *trans*form spectra was done with EXAFSPAK suite.

2.2.4. *Catalytic activity testing*

Two different naphthenic ring compounds, decahydronaphthalene (decalin) and 1,2,3,4-tetrahydronaphthalene (tetralin), were used in this study. Tetralin (98+%) and decalin (a mixture of *trans*- and *cis*-decalin, ratio 63/37) were purchased from Acros. Pure *trans*-decalin (99%) and *cis*-decalin (99%) from Alfa Aesar were also tested to study the reactivity of the different isomers in the ring-opening reaction.

The catalytic activity measurements were carried out in a continuous fixed-bed stainless-steel 3/8-inch (o.d.) reactor. In each run, 0.2 g of catalyst was diluted with SiC to make the volume of the catalyst bed 2.25 ml. The experimental conditions were chosen as follows: (i) the decalin ring-opening reaction was performed at 533 K and 2 MPa with a H_2:decalin molar ratio of 65; (ii) the pulse experiments were carried out in the temperature range 533–600 K, at a total pressure of 0.2 MPa; (iii) the tetralin ring-opening reaction was conducted at 600 K; 2 MPa; H_2:tetralin molar ratio of 60. Space velocities were systematically varied by changing either the catalyst amount or the hydrocarbon feed rate. To avoid running reactions at a temperature higher than the reduction pretreatments the reduction was selected according to the reaction temperature range. That is, prior to the reaction with decalin, the catalysts were reduced in hydrogen (100 ml/min) at 573 K for 2 h. For the tetralin test the catalysts were reduced at 673 K.

A set of experiments was conducted with physical mixtures of catalysts on the same reaction system described above. The catalysts used in the mixtures were a conventional 1.0 wt% Pt/SiO_2 prepared by incipient wetness impregnation and a pure HY3 zeolite. Four different physical mixtures were prepared. In two of them, the different catalysts were segregated in separate beds. In the system identified as Pt $\gg$ HY, the Pt/SiO_2 catalyst was placed in front of the HY3 zeolite. By contrast, in the system identified as HY $\gg$ Pt, the Pt/SiO_2 catalyst was placed after the HY3 zeolite. For the other two systems, the Pt/SiO_2 catalyst and the HY were intimately mixed in two different ratios Pt + HY (1:1) and Pt + HY (1:2).

In the pulse experiments, 0.05 g of catalyst was placed in a stainless-steel tube between glass beads to keep the catalyst at the center of the heated zone. Before sending the hydrocarbon pulses, the catalyst was pretreated in a 100 ml/min flow of pure H_2 at 573 K for 1 h and then heated to the selected reaction temperature (593 or 630 K). Microliter pulses of either pure *cis*-decalin or pure *trans*-decalin were sent over the catalyst and the products analyzed in a GC with FID detector.

2.2.5. *Product analysis*

The products were analyzed online by a HP5890 II gas chromatograph with FID detector using an HP-5 boiling-point type column and trapped by cooling water. Two gas chromatographs with mass spectrometer detectors (Shimadzu QP5000 and GCD HP 1800A) were used to identify all the products formed during the reaction. More than 200 compounds were identified in the GC-MS analysis. The assignment of so many products is not a straightforward task and it must be stressed how much attention should be put into this effort to obtain a reliable analysis. To assign and quantify each product, a combination of residence time, cracking pattern, and comparison with GC standards was used. For each assignment, the relative boiling points, retention times, and cracking patterns from the NIST library were evaluated. The following Supelco GC standards were used *cis*- and *trans*-decalin, benzene, butylcyclohexane, cyclohexene,3-methyl-6-(1-methylethyl), isoparaffin mix, *n*-paraffin mix (C5–C8 and C7–C10), aromatics mix, and naphtha standard. In addition to these comparisons we conducted reality checks to be sure that the assigned compound behave as expected. For example, an olefin should decrease when the hydrogen pressure increases, as well as when Pt was incorporated in the HY catalyst. At the same time, the corresponding paraffin with the same skeletal structure should increase accordingly. To corroborate the analysis of the olefins present in the sample, the Bromine Index test was conducted on a couple of samples, one from the Pt/HY3 catalyst, the other from HY3 catalyst. The former showed less than 1 wt% olefins, while the latter showed about 8 wt%, a trend that was in reasonable agreement with the results obtained from the GC analysis.

For the sake of clarity, we have grouped these products according to the number of carbon atoms in the molecule and in terms of the carbon skeleton reaction involved. These groups areas follows:

(a) Cracking products. They contain two fractions, C1–C5 (mostly isobutane, and 2-methylbutane) and C6–C9 (such as methylcyclopentane, methylcyclohexane, benzene, toluene, xylenes, ethylbenzene, ethylcyclohexane, and dimethylbenzene).
(b) Ring contraction (RC) C10 products. They are characterized by the presence of C5 rings fused to C6 rings (methylindanes, methylbicyclo[4.3.0]nonanes), two rings connected together (such as 3,7,7-trimethylbicyclo-[4.1.0]heptane, dimethylbicyclo[3.3.0]octanes, methylbicyclo[3.3.1]nonanes) and two C5 rings (1,1′-bicyclopentyl and spiro[4.5]decane).
(c) Ring-opening C10 products (alkyl/alkenyl cyclopentanes, alkyl/alkenyl cyclohexanes, or cyclohexenes or benzenes). Some products are butylcyclohexane, butylcyclohexene, butylbenzene, 4-methyl-1-(1-methylethyl) cyclohexene, 1-methyl-4-(1-methylethylid) cyclohexane, etc. However, it must be noted that within the RO products such as 1-methyl-4-(1-methylethyl) cyclohexane clearly have undergone not only RO, but also a transalkylation step [3].
(d) Dehydrogenation products (tetralin and naphthalene).

3. Results and discussion

3.1. Characterization of fresh catalysts

Table 1 shows the density of acid sites as determined from the integration of the NH_3 TPD and from FTIR of adsorbed pyridine. A clear trend indicates that, as expected, the density of acid sites (both Brønsted and Lewis) increased after each subsequent ion exchange with ammonium chloride. An interesting point to draw attention to is that the impregnation with metals leads to a significant loss in the number of acid sites, not only Brønsted, which may result from direct anchoring on proton sites, but also Lewis.

The EXAFS analysis of the reduced Pt/HY3 at 673 K results in a coordination number for Pt–Pt of 7.0, indicating a good dispersion of the metal and an average particle size that would fit in a sphere of about 1.1 nm. This coordination number compares well with other well-dispersed Pt clusters on HY zeolites reported in the literature [17]. However, De Graaf et al. [18] have shown that for a 1 wt% Pt loading, one can only expect to have all of the Pt inside the HY zeolite structure when using ion exchange with tetra-amine precursors and a heating rate as low as 0.2 °C/min. In that case, coordination numbers of the order of 5.5 have been obtained. Since the preparation method employed in the present contribution is not optimized we may expect the typical bimodal distribution, with a fraction of small metal clusters inside the HY zeolite structure and a fraction outside forming relatively large particles. Therefore, the coordination number of 7.0 represents an average between these two types of Pt particles, more than a typical particle size.

3.2. Catalytic activity measurements

3.2.1. Conversion of decalin over HY and metal-HY catalysts

Table 2 shows the product distribution obtained on the different catalysts at 2 MPa and 533 K with a decalin feed (*trans*/*cis* feed ratio: 63/37) after 75 min and 155 min on stream. The initial conversion (not shown) paralleled the trend in acid density (i.e., HY1 < HY2 < HY3). However, as shown in Table 2 the deactivation patterns were significantly different over the different catalysts and as a result, after 75 min on stream, the conversion on the zeolite with the highest acidity (HY3) was already lower than that on HY2. To investigate the effect of deactivation on the product distribution, the flow reactor that we have used in this work is more appropriate than the batch reactor used in recent studies [8] as it allows one to follow the overall conversion and product distribution as a function of time on stream. For example, the rapid deactivation observed on catalyst HY3 is paralleled by a rapid decrease in the yield of C1–C5 products, which are dominant during the first few minutes on stream, but decrease to very low values after 2 h.

Table 1
Characterization of acidity

Sample	Total acidity[a]	Acidity[b] (μmol Py/g)					
	Amount of desorbed NH_3 (μmol/g_{cat})	Brønsted (1545 cm^{-1})			Lewis (1445 cm^{-1})		
		523 K	623 K	673 K	523 K	623 K	673 K
HY1 (1)	665	232	222	199	223	209	34
HY2 (2)	1487	515	475	394	525	377	212
HY3 (3)	1670	628	610	501	581	461	289
Pt/HY3	1141	452	398	301	377	313	224

1, NaY after 1st ion-exchange with NH_4Cl; 2, NaY after 2nd ion-exchange with NH_4Cl; 3, NaY after 4th ion-exchange with NH_4Cl.

[a] Total acidity measured by TPD of NH_3.

[b] Acidity measured by adsorbed pyridine at different temperatures.

Table 2
Conversion of decalin on HY zeolite

	Feed	HY1		HY2		HY3		Pt/HY3	
TOS		75 min	155 min	75 min	155 min	75 min	155 min	75 min	155 min
trans-Decalin (wt%)	63.0	73.9	73.5	33.3	47.2	54.2	63.8	65.5	66.2
cis-Decalin (wt%)	37.0	15.2	15.7	1.8	3.1	4.9	6.5	5.8	6.4
Conversion[a] (%)	–	10.9	10.9	64.9	49.7	40.8	29.8	28.7	27.4
Products		Yield (wt%)		Yield (wt%)		Yield (wt%)		Yield (wt%)	
C1–C5	–	0.6	0.5	22.2	16.2	10.4	3.5	1.7	1.7
C6–C9	–	0.2	0.3	9.6	3.8	3.4	1.9	4.3	3.7
C10 products		10.2	10.0	33.1	29.6	27.1	24.4	22.7	22.0
Alkylcyclonaphthenes and alkylcyclobenzenes	–	9.4	9.0	19.1	19.0	19.1	15.1	11.8	11.1
Ring contraction products	–	0.1	0.2	14.0	10.6	8.0	9.3	10.9	10.9
Tetralin and naphthalene	–	0.7	0.8	0.0	0.0	0.0	0.0	0.0	0.0

Reaction conditions: feed; decalin; 2 MPa, 533 K, LSV $= 1.89\ h^{-1}$, H_2 to feed molar ratio = 65.

[a] Conversion based on *trans*-decalin and *cis*-decalin.

The addition of Pt to the acidic zeolite HY3 results in the loss of an important fraction of acid sites (see Table 1). As a consequence, the lower amount of cracking products and initial overall conversion observed on the Pt/HY3 compared to the proton-form zeolite HY3 is not unexpected. In addition, it was observed that the presence of Pt greatly enhanced the stability of the catalyst since the fast deactivation of the HY3 catalyst was not observed for the Pt/HY3. In parallel to the rapid deactivation of HY3 catalyst a significant drop in the cracking products is observed on this catalyst as a function of time on stream. Moreover, the yields of C10 products of higher interest to this study, RC and RO, are higher for the catalyst of higher acidity, but they decrease as the catalysts deactivate. As a result, the catalyst with intermediate acidity is after a few hours the most effective for C10 product yield. Fig. 1 illustrates the variation of overall conversion as a function of time on stream for all the catalysts; clearly, the activity was lower for the two catalysts with lower acidity, HY1 and Pt/HY3, but at the same time the deactivation was much less pronounced for these catalysts than for those with higher acidity density.

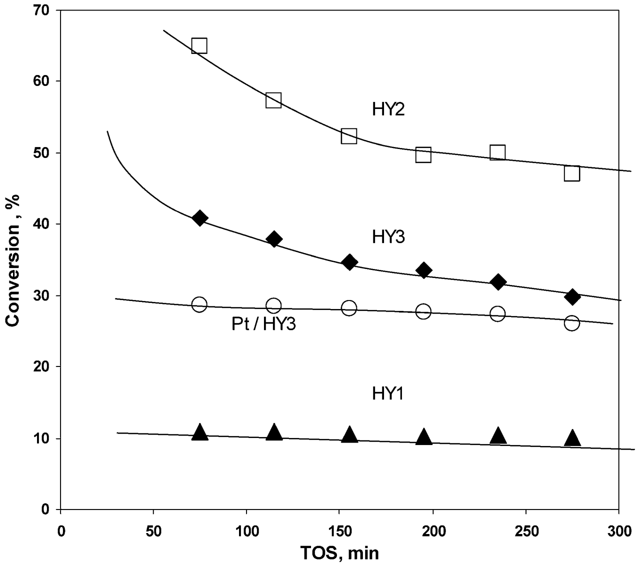


Fig. 1. Total conversion of decalin on various catalysts. Reaction conditions: 2 MPa, 533 K, H_2 to feed molar ratio = 65.

An interesting change in the *trans*/*cis* decalin ratio was observed in the product compared to that in the feed (63/37). In all cases, as shown in Table 2, this ratio was observed to increase significantly. The preferential disappearance of *cis*-decalin may be due to two causes, (a) *cis*-to-*trans* isomerization or (b) higher reactivity of *cis* that makes it react faster than *trans*. Both effects may be present, although the latter seems to be dominant on these catalysts. The *trans*/*cis* ratio was as high when using the Pt/HY catalyst as when using the proton form of HY zeolites. However, as previously shown [19], the *cis*-to-*trans* isomerization should be more significant in the presence of Pt/HY than on the bare HY zeolites, which indicates that the *cis*-to-*trans* isomerization is not the dominant factor in determining the *trans*/*cis* decalin ratio.

The results of Table 2 strongly suggest that on all catalysts most of the conversion occurs on the *cis*-decalin, the reactant that is preferentially consumed. A plausible explanation is that the reactivity of *cis*-decalin for cracking and ring opening on HY is much higher than that of *trans*-decalin. In fact, differences in the reactivity of the two isomers have been observed previously by other authors [20,21]. As demonstrated by Mostad et al. [20] the difference in reactivity between *cis*- and *trans*-decalin is much more obvious for zeolite Y than for amorphous silica–alumina. The preferential reactivity might be related to the greater ability of the *cis* isomer to penetrate the Y zeolite pore (about 0.74 nm) due to its slightly smaller molecular dimensions and, most importantly, its higher conformational mobility.

It is also reasonable to expect that the *cis* isomer can generate the surface reaction intermediate more easily than the *trans* isomer. The *trans* form has more hindered C–H bonds than the *cis* form; this steric difference may account for the lower reactivity. If the reaction intermediate has the positive charge on the tertiary carbon, it will be the same for both isomers. If that is the case, with *trans* more stable than *cis*, the difference in energy with the reaction intermediate (activation energy) would be higher for *trans*-decalin.

The reactivity difference manifests again in Fig. 2 for the ring-opening reaction, which shows the product distribution for the reaction of the 63/37 *trans*/*cis*-decalin feed as a function of the space time (W/F). At low W/F, the amount of *cis*-decalin dramatically decreases with increasing W/F. Although some of the *cis* conversion may have been isomerization to *trans*, most of the *cis*-decalin consumption is mirrored by the increase in the amount of C10 ring-opening products. Beyond a certain W/F (i.e., ∼ 0.45 h), increasing the reactor size results in selectivity losses as secondary cracking products begin to be formed in larger quantities. It is also seen that the *trans*-decalin does not decrease at low W/F, but rather slightly increases due to *cis*-*trans* isomerization and only decreases at very high W/F, when the cracking products begin to appear. From these trends it seems that *cis*-decalin mainly converts into RO products while *trans*-decalin is much less reactive, but when it reacts it does it unselectively to multiple cracking. However, the parallel *cis*-to-*trans* isomerization may mask the contribution of the direct *trans* conversion. Therefore, it is important to use isomerically pure *cis*- and *trans*-decalin feeds to compare the reactivity of the two isomers. Those experiments are shown below in Section 3.2.2.

To further analyze the evolution of RC and RO with overall conversion, we summarize in Fig. 3 a larger number of data points obtained on the three HY catalysts at various W/F and at various times on stream. It can be observed that both the RC and the RO products initially increase in concentration as a function of conversion, but at some point the evolution of RC products levels off and finally decreases, while the concentration of RO products keeps increasing. As proposed by Kubicka et al. [8], the reactivity of RC products is much higher than that of RO products, either due to a higher strain in the five carbon ring or due to a larger number of tertiary carbons in the molecule. Therefore, it is not surprising that as conversion increases, RC products are gradually converted into RO products. Fig. 4 shows that the evolution of the RC/RO ratio follows the same pattern as a function of conversion for all the HY catalysts, whether conversion has been varied by increasing space–time (W/F) or by catalyst deactivation.

An interesting change in product distribution is observed in Fig. 4 when Pt is added to the HY zeolite. Although the RC/RO ratio still decreases with overall conversion the absolute value of this RC/RO ratio for any given conversion is higher on the metal-containing catalyst than on any of the proton-form zeolites. The metal-containing Pt/HY3 catalyst contains a significantly lower acidity density than the pure HY3 zeolite. This lower acidity density may account for the lower amount of cracking products. However, the high RC/RO ratio indicates that the presence of the metal favors the RC step while inhibiting the RO. A possible explanation of this effect is that a partial dehydrogenation over the metal would accelerate the activation of decalin, but at the same time, an enhanced hydrogen transfer would reduce the lifetime of surface carbenium ions, allowing the desorption of RC products and preventing their further reaction to RO products. An interesting comparison is made below in Section 3.2.4 with physical mixtures in which the Pt metal is not inside the zeolite. In that case, the RC/RO ratio is as low as for the proton-form zeolite alone, which supports the idea that the change in RC/RO ratio is due to enhanced hydrogen transfer inside the zeolite.

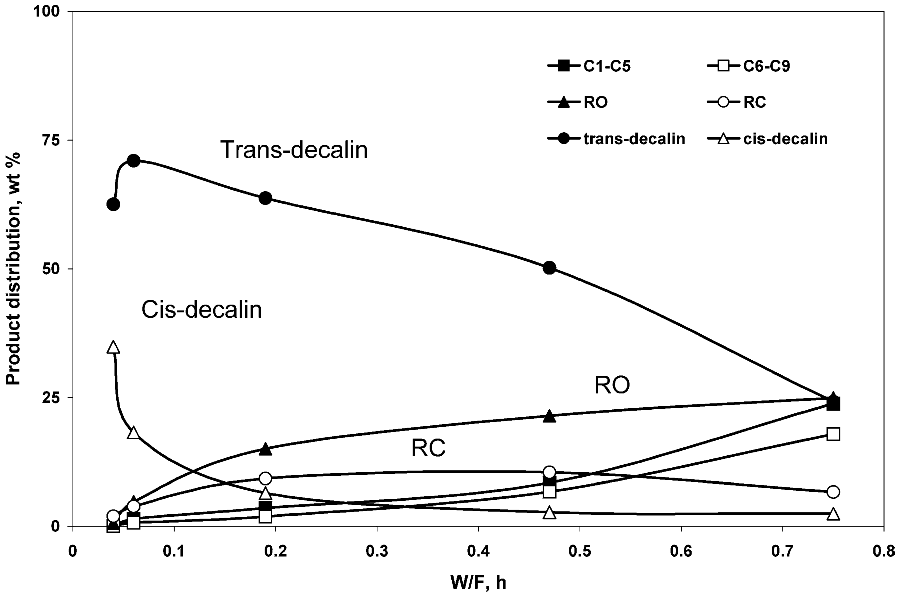


Fig. 2. Product distribution of decalin ring opening on HY3 at different space velocities. Reaction conditions: 2 MPa, 533 K, H_2 to feed molar ratio = 65. After time on stream = 155 min.

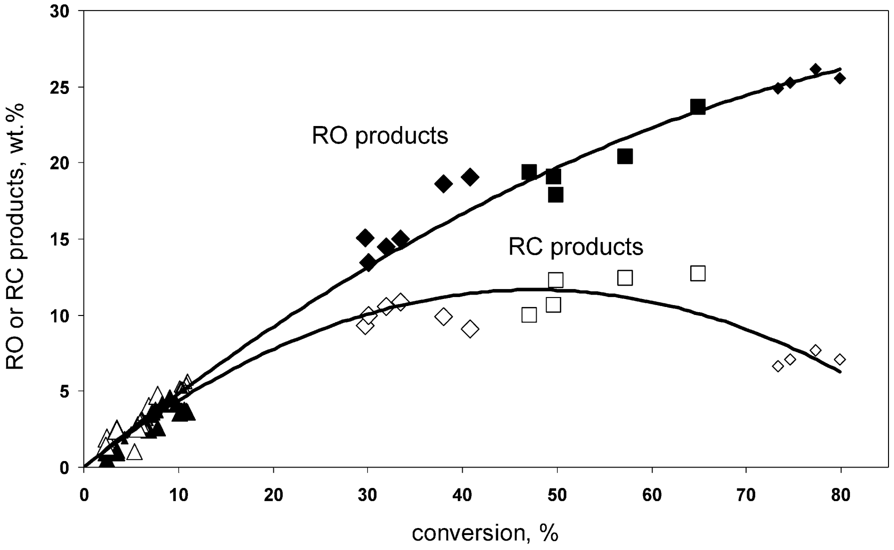


Fig. 3. RO and RC products of decalin ring opening on various catalysts at varying conversions (both by space times and time on stream). Squares: HY2; diamonds: HY3; triangles: HY1. Reaction conditions: 2 MPa, 533 K, H_2 to feed molar ratio = 65.

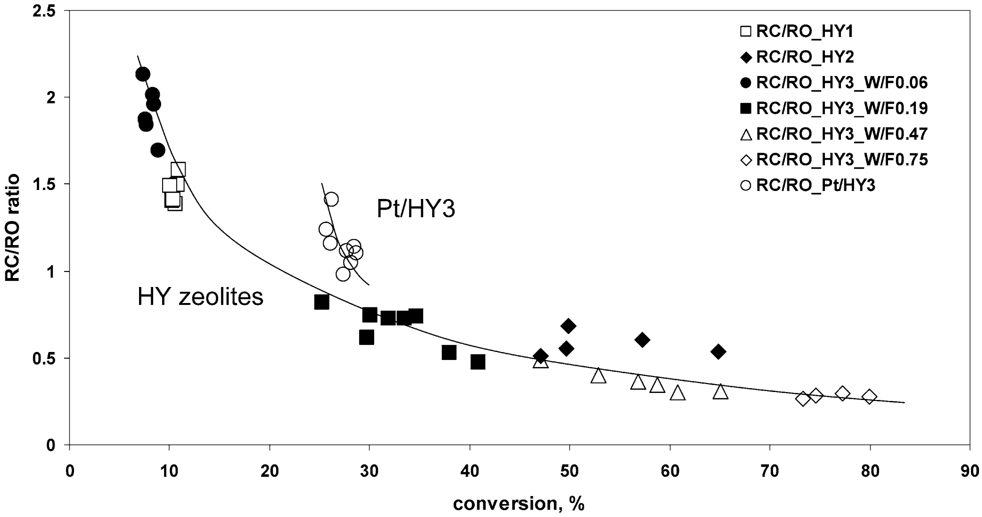


Fig. 4. RC/RO ratio of decalin ring-opening on HY zeolites and Pt/HY3 at different conversions. Conversions were varied by changing space time and time on stream. Reaction conditions: 2 MPa, 533 K, H_2 to feed molar ratio = 65.

According to the reaction scheme proposed by Corma et al. [3], RO products could be obtained either by direct opening of the decalin molecule via protolytic cracking (PC) or via a secondary cracking of RC products. In Fig. 5, we report the evolution of two relevant RO and RC products as a function of conversion on catalyst HY3. It can be seen that while the RC product, methylbicyclo[3.4.0]nonane appears as a primary product, the RO product butylcyclohexane behaves as a secondary product. It must be noted that butylcyclohexane can only be formed by two alternative paths, either as a primary product by direct PC followed by hydride transfer and desorption [3] or as a secondary product from the opening of methylbicyclo[3.4.0]nonane. The observed trend as a function of conversion and the zero derivative at zero conversion indicate that most of butylcyclohexane is formed as a secondary product from the cracking of the methylbicyclo[3.4.0]nonane, which by contrast, starts decreasing as the butylcyclohexane increases. In fact, RC products are generally considered primary products. However, in doing this type of analysis one must take into account the possibility that, by the time the molecule leaves the zeolite, it may have already undergone secondary reactions. For example, the evolution of 1-methyl-4-(1-methylethenyl) cyclohexane looks as if it were a primary product. However, the formation of this RO product obviously requires a complicated skeletal rearrangement that may includes ring contraction, ring opening, and skeletal isomerization or *trans*-alkylation. It was observed that even at very low conversions, the yield of the RO product was significant. Therefore, it appears that in this system it is difficult to observe truly primary products, even when running at very low conversions.

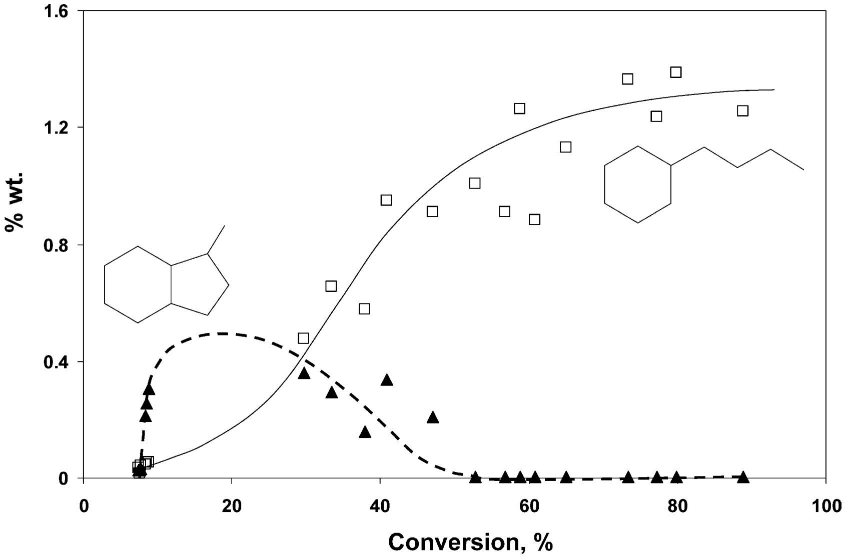


Fig. 5. Yield of two relevant products as a function of conversion. Solid triangles: methylbicyclo[4.3.0]nonane; open squares: butylcyclohexane.

3.2.2. *Conversion of isomerically pure cis- and trans-decalin*

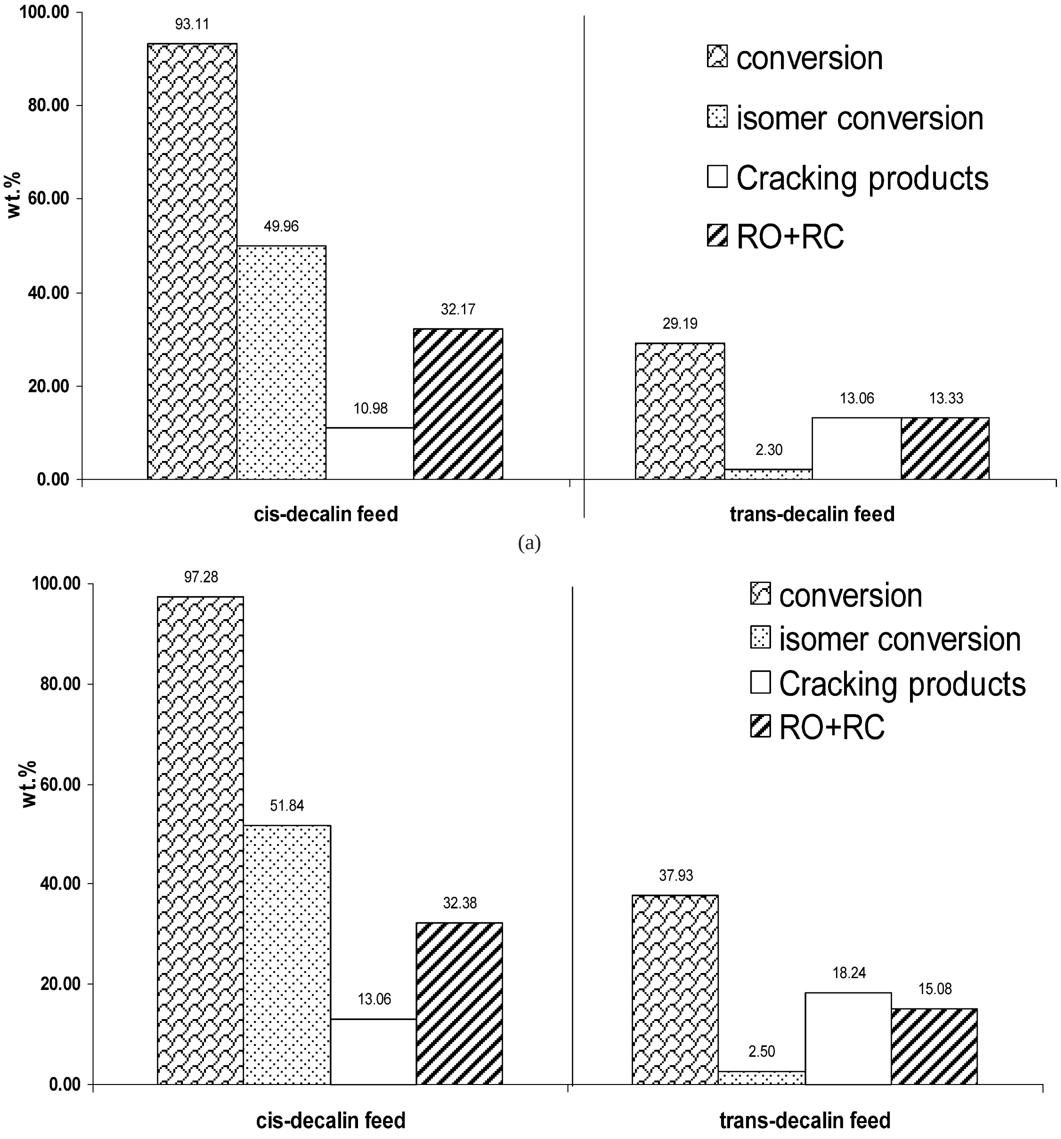
As noted above, the comparison of the intrinsic activity of the two decalin isomers may be obscured by the *cis*-to-*trans* isomerization reaction that occurs in parallel. Therefore, in order to compare their reactivities we measured the conversion of isomerically pure *trans*- and *cis*-decalin feeds at 533 K and 2 MPa on the HY3 and Pt/HY3 catalysts in the flow reactor. The observed inequalities in activity and selectivity were indeed remarkable for both HY and Pt/HY catalysts. The overall conversion for the two different pure feeds is compared in Figs. 6a and b, which unambiguously demonstrates that the *cis*-decalin is not only much more reactive than *trans*-decalin, but also more selective to C10 ring-opening products. In fact, the dominant products from *trans*-decalin were cracking products (C1–C9), rather than C10 products.

To confirm that the difference between the two isomers is related to the reactivity of the molecules on these particular catalysts, rather than to an indirect effect, such as a different degree of coking and deactivation, we conducted another comparison in a pulse reactor over clean catalysts at low pressures (0.2 MPa). In these experiments, micropulses of pure *trans*-decalin and pure *cis*-decalin were sent over the proton-form of HY3 zeolite. The product distributions for these experiments are shown in Table 3. High conversions were observed for pure *cis*-decalin on the HY3 catalyst at 593 and 630 K, 83 and 92%, respectively. By contrast, very low conversions, 13 and 27%, were obtained with *trans*-decalin under the same conditions, that is, 593 and 630 K, respectively. At the lower temperature, the overall yield to C10 ring opening from *cis*-decalin was almost 30 times higher than that from the *trans* isomer. As the temperature increased, the selectivity to RO products decreased as secondary cracking became more dominant. Nevertheless, the important conclusion from these studies is that regardless of the presence or absence of metal in the catalyst, or of the pressure at which the reaction takes place, reactive of *cis*-decalin on HY-based catalysts is clearly superior to that of *trans*-decalin.

3.2.3. *Conversion of tetralin*

Due to the presence of the aromatic ring, tetralin is more difficult to convert than decalin. Corma et al. [3] have seen activity differences between tetralin and decalin on HY zeolites, but since their study was conducted at 723 K, the differences were not so dramatic as those seen here at lower temperatures. In fact, while the conversion measurements on decalin were conducted at 533 K, those with tetralin had to be conducted at 600 K to get comparable conversions. As shown in Table 4, the most obvious contrast with the decalin study (Table 2) is the large increase in activity observed in the presence of a metal. While in the case of decalin conversion, the addition of metal causes a decrease in initial conversion, when tetralin was used, and the presence of the metal greatly increased the conversion. In fact, despite the lower acidity density, the overall conversion on the Pt/HY3 catalysts was at the same W/F more than four times that on HY3. Even when subtracting the conversion to hydrogenation products, the conversion is significantly higher than on HY3. The obvious explanation for this increase is that the metal catalyzed hydrogenation that converts tetralin into decalin, which is then further converted as seen above. In agreement with our findings, Arribas and Martinez [9] have concluded that the initiation step for the hydrocracking of naphthalenes on Pt/HY is the sequential hydrogenation of naphthalenes to tetralins and decalins on the metal, followed by formation of carbocations on the Brønsted sites of the zeolite, which lead to cracking and RO products [22].

This sequence is demonstrated in Fig. 7, which shows the product distribution for the reaction of the tetralin feed as a function of space–time (W/F) over Pt/HY. This graph



(a)

(b)

Fig. 6. Pure *cis*- and *trans*-decalin in flow mode on (a) HY3 and (b) Pt/HY3. Reaction conditions: 2 MPa, 533 K, LSV = 1.89 h^{-1}, H_2 to feed molar ratio = 65 after time on stream = 155 min.

Table 3
Conversion of pure *cis*- and *trans*-decalin in pulse reactor on HY3 zeolite. Total pressure 0.14 MPa

	593 K		630 K	
	cis-Decalin	*trans*-Decalin	*cis*-Decalin	*trans*-Decalin
trans-Decalin (wt%)	8.78	87.49	7.00	73.37
cis-Decalin (wt%)	17.49	0.33	8.53	0.01
C1–C9 (wt%)	53.74	10.78	62.14	21.29
RO (wt%)	11.66	0.57	11.94	1.40
RC (wt%)	7.57	0.68	9.13	3.12
Tetralin (wt%)	0.44	0.15	1.03	0.81
Naphthalene (wt%)	0.31	0.00	0.23	0.00

clearly establishes that on this catalyst the only primary products from tetralin are *cis*- and *trans*-decalin. Regarding the variation of the *trans*/*cis*-decalin ratio, it is also seen in Fig. 7 that both isomers start with identical slopes, at W/F near zero, but very quickly the slope for the *cis*-decalin yield decreases while the *trans*/*cis* ratio increases. At this point, the secondary products appear (i.e., cracking, ring contraction, and ring opening). The concentration of *trans*-decalin in the reactor keeps increasing with W/F up to high W/F values, at which point, its decrease is accompanied by an

Table 4
Conversion of tetralin.

	HY1	HY2	HY3	Pt/HY3
Tetralin conversion (%)	16.34	16.76	23.95	92.55
Products	Yield (wt%)	Yield (wt%)	Yield (wt%)	Yield (wt%)
C1–C5	0.00	0.28	1.93	1.37
C6–C9	5.35	4.42	7.63	4.98
C10 products				
Ring opening products	2.95	4.31	5.49	14.99
Alkylcyclo compounds	0.72	1.53	0.79	14.13
Alkylbenzene	2.23	2.78	4.70	0.86
Ring contraction products	1.86	2.49	2.96	19.67
trans-Decalin	1.05	1.69	0.79	44.35
cis-Decalin	0.48	0.46	0.34	6.20
Naphthalene	4.64	3.10	4.81	0.99

Reaction conditions: feed, tetralin; 2 MPa, 598 K, after 155 min.

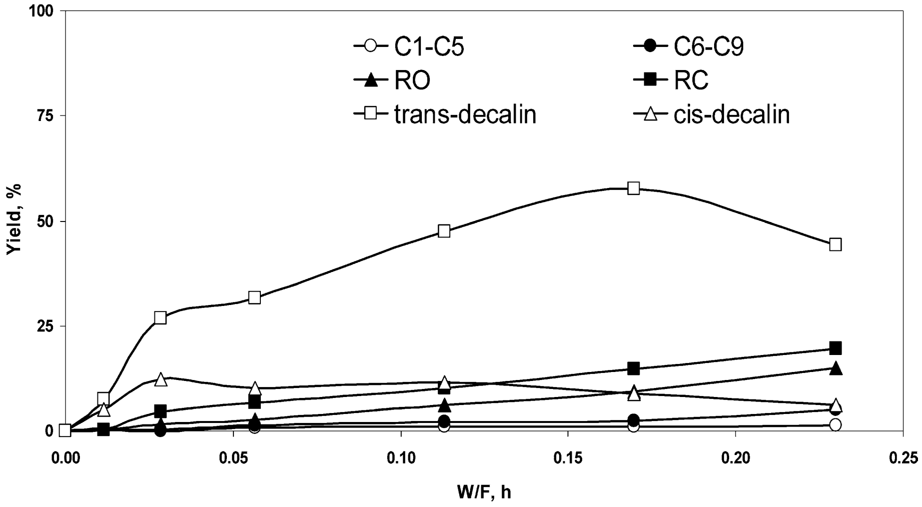


Fig. 7. Product distribution of tetralin ring opening on Pt/HY3. Reaction conditions: 2 MPa, 598 K, H_2 to feed molar ratio = 60 after 155 min.

increase in light cracking products. The different trends observed for *cis*- and *trans*-decalin can be explained, as discussed above, in terms of the *cis*-to-*trans* isomerization and the higher reactivity of the *cis* isomer.

Another interesting contrast observed in Table 4 is that when tetralin is used as a feed instead of decalin the production of naphthalene greatly increases, particularly on the HY zeolites without metals. Naphthalene most probably results from bimolecular reactions in which two tetralin molecules are converted into naphthalene and decalin or RO products, as previously proposed [23]. Alternatively, as suggested by Corma et al. [3] it can arise from a hydrogen transfer between tetralin and the adsorbed carbenium ions, in agreement with earlier work [24]. Interestingly, Townsend and Abbot [23] in a study conducted with tetralin on HY at atmospheric pressure and without hydrogen addition found that the decalin/naphthalene ratio was much lower than what we observe here under high hydrogen pressure. It is then possible that the added hydrogen participates on the hydrogen transfer steps.

Fig. 8 shows the evolution of the RC/RO ratio as a function of conversion for Pt/HY and HY3. On the Pt/HY3 catalyst, different initial conversions were obtained by varying W/F. Clearly, the RC/RO ratio is much higher for the Pt/HY catalyst than for the HY catalysts. At the same time, it is observed that the RC/RO ratio greatly increases as the catalyst deactivates.

As indicated above for the decalin reaction, the high RC/RO ratio indicates that the presence of the metal enhances the RC step more than the RO step. The generation of olefins accelerates the activation of decalin, but at the same time, the hydrogen transfer enhanced by the presence of Pt can reduce the lifetime of the surface intermediates, allowing the desorption of RC products and preventing their subsequent reaction to RO products.

3.2.4. Tetralin conversion on physical mixtures and segregated beds of Pt/SiO$_2$ and HY catalysts

To discern the role of the individual functions of the catalyst (metallic and acidic) we devised a series of experiments to react tetralin over physical mixtures of catalysts

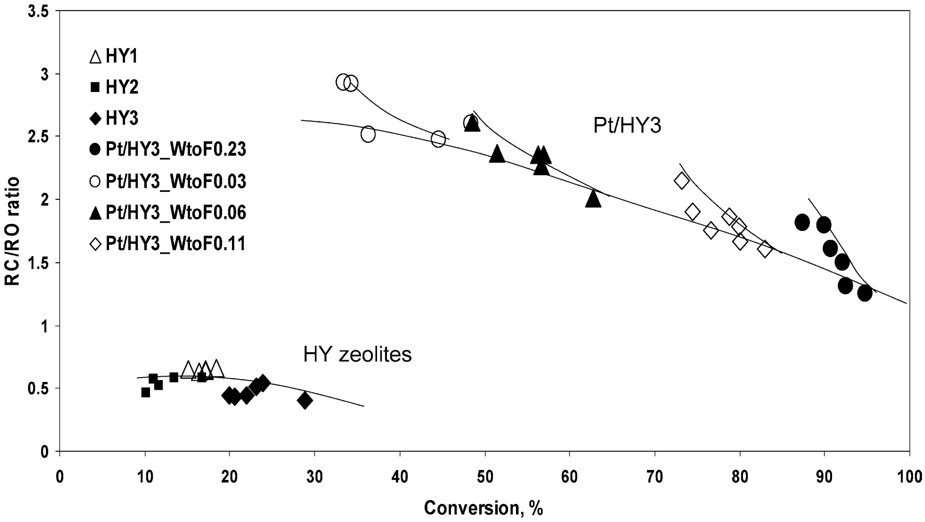


Fig. 8. RC/RO ratio of tetralin ring opening on HY3 and Pt/HY3. Different symbols indicate runs conducted at different W/F. Reaction conditions: 2 MPa, 598 K, H_2 to feed molar ratio = 60.

Table 5
Conversion of tetralin on physical mixtures of Pt/SiO_2 and HY catalysts.

	HY	Pt ≫ HY	HY ≫ Pt	Pt + HY, 1:1	Pt + HY, 1:2	Pt/HY
mmoles of H^+ [a]	0.33	0.20	0.20	0.20	0.31	0.22
mmoles of Pt	0.00	0.62	0.62	0.62	0.48	1.03
Tetralin conversion (%)	11.84	97.52	91.33	86.42	98.66	91.38
Products	Yield (wt%)	Yield (wt%)	Yield (wt%)	Yield (wt%)	Yield (wt%)	Yield (wt%)
C1–C5	ND	ND	ND	ND	ND	ND
C6–C9	0.23	0.56	0.46	0.24	0.54	0.16
C10 products						
Ring opening products	3.10	8.79	3.20	5.11	12.59	12.40
Alkylcyclo compounds	0.90	8.70	2.69	4.85	12.42	11.07
Alkylbenzene	2.20	0.09	0.51	0.25	0.17	1.32
Ring contraction products	2.26	4.13	2.50	3.34	7.08	12.73
trans-Decalin	1.05	75.31	70.46	62.04	70.63	55.43
cis-Decalin	0.61	7.06	14.01	14.48	7.76	9.69
Naphthalene	4.59	1.68	0.70	1.21	0.05	0.98

Reaction conditions: feed, tetralin; 2 MPa, 598 K, after 420 min.

[a] Based on TPD of NH_3.

and sequential catalyst beds. A Pt/SiO_2 sample was used to represent the monofunctional metallic catalyst and the proton-form HY3 zeolite was used as the monofunctional acid catalyst. In one of the sequential bed reactors, the 1 wt% Pt/SiO_2 catalyst was placed in front of the HY3. In the other, the 1 wt% Pt/SiO_2 bed was placed after the HY3 bed. In addition, two other samples were prepared by physically mixing the 1 wt% Pt/SiO_2 and HY3 catalysts in two different Pt/SiO_2:HY ratios, 1:1 and 1:2. The product distributions obtained on the different samples for the reaction of tetralin at 600 K and 2 MPa after 7 h on stream are summarized in Table 5. It must be noted that in this analysis, as opposed to those described above, only the liquid was collected in a cold trap, but the light products were not measured. Therefore, Table 5 shows the C1–C5 range as not determined (ND).

As noted above, the reaction on the HY catalyst alone produces alkylbenzenes as the major RO products together with naphthalene, which results from the hydrogen transfer from tetralin to the surface carbenium ions. Over this catalyst, the production of decalin is minimal; therefore, we can envision a surface carbenium ion which still keeps its original aromatic ring intact. A hydrogen transfer step from tetralin should result in the evolution of alkylbenzene and dehydrogenation of tetralin. It is interesting to compare the production of alkylbenzenes from pure HY catalysts as opposed to alkylcyclohexanes that are observed when Pt is present. This important disparity can be due to two possible causes. One of them is that alkylbenzenes are formed, but later hydrogenated over the metal. The other is that they are not formed; that is, the carbenium ion intermediates do not contain the aromatic ring. The experiments that we have designed are most appropriate to differentiate these alternatives. In the run in which Pt is placed before the HY (Pt ≫ HY) hydrogenation over Pt can only occur before the generation of the carbenium ions. Therefore, the lack of alkylbenzenes cannot be due to secondary hydrogenation. Rather, the clear increase in the concentration of decalin resulting from hydrogenation of tetralin on the first bed causes RO products formed in the subsequent HY bed that do not contain aromatic rings. That is, the carbenium ion is formed from decalin and the RO products are alkylcyclohexanes/enes. When Pt is present, any olefin product from the RO is rapidly hydrogenated under these conditions. Olefins only appear in small quantities at temperatures above 320 K and lower pressures.

By contrast, in the run in which HY precedes the Pt bed (HY $\gg$ Pt) we expect that in the first bed alkylbenzenes are formed, but later, they are effectively hydrogenated to alkylcyclohexanes over the Pt catalyst. In fact, it is observed that very small amounts of alkylbenzenes are seen after the Pt bed. Since the reactivity of decalin toward RO on HY is much higher than that of tetralin, the remarkable increase in the yield of RO products is simply due to the initial hydrogenation of tetralin to decalin in the case of the Pt-first system (Pt $\gg$ HY).

Another important question that can be addressed on the basis of this set of experiments is why the disappearance of *cis* is so much faster than that of *trans*, as seen in Figs. 2 and 7. As noted above, this difference is due to two reasons. One is the isomerization of *cis* to *trans*, and the other is the higher reactivity of *cis* compared to *trans*. The two effects are clearly apparent in the results presented in Table 5. In the first place, it is seen that the production of decalin from tetralin is, at least, two orders of magnitude slower on HY than on Pt. At the same time, the *cis*-to-*trans* conversion is also slower. In agreement with this result, Lai and Song [19] have observed that the *cis*-to-*trans* isomerization over Pt- and Pd-modified zeolites is much faster than over proton-form zeolites. The *trans*/*cis* ratio obtained on HY is only 1.7. On the metal, the *trans*/*cis* ratio should increase. We have previously shown [25] that, in the decalin produced by hydrogenation of tetralin on pure Pt catalysts at low conversions, the *trans*/*cis* ratio is about 1.0 and remains fairly constant up to tetralin conversion levels of 80% and above. At high conversions, the *trans*/*cis* ratio increases to about 4–6. In the two-bed reactor (HY $\gg$ Pt) one expects a low conversion to decalin in the first part (HY) while on the second part of the reactor (Pt/SiO_2) initial hydrogenation produces a 1:1 mixture of *cis* and *trans*, followed by isomerization of *cis*-to-*trans*, as indicated by the observed *trans*/*cis* ratio of about 5. By contrast, in the two-bed reactor (Pt $\gg$ HY), we expect a ratio of about 5 after the first part (Pt/SiO_2) but little *cis*-to-*trans* isomerization in the second part (HY). Therefore, the very high *trans*/*cis* ratio observed, which approaches the equilibrium value of 11, is due to the preferential consumption of *cis* by the RO reaction. This conclusion is in agreement with Mostad et al. [20] who first proposed that the conversion of *cis* to other products was higher than *cis* to *trans*, but much higher than *trans* to other products.

Another interesting comparison is the concentration of RC products obtained over Pt/HY compared to that obtained on the physical mixtures Pt + HY. The catalyst in which Pt is directly supported on the HY zeolite, with an important fraction of metal deposited inside the zeolite porous structure, exhibits a very high concentration of RC products. As shown in Fig. 8, the RC/RO ratio on the Pt/HY catalyst for an initial tetralin conversion of 83% is 1.6. By contrast, as shown in Table 5 this ratio over the physical mixture Pt + HY (1:1) is only 0.65 at a tetralin conversion of 86%. The analysis methods used in Fig. 8 and Table 5 were somewhat different. In the former case, the analysis was done on-line so it represents the instantaneous composition, while on the latter, only the liquid was collected over a period of several hours, so the data represent the average over that period and does not contain the lighter products. However, the difference in the two catalysts, i.e., Pt/HY and the physical mixture Pt + HY (1:1), is still obvious from the results of Table 5, since the RC/RO ratio for Pt/HY at a conversion of 91% was 1.03.

We have previously noted that the RC/RO ratio is much lower for the proton-zeolites without metal. Here, it is demonstrated that this enhancement is only observed when Pt is inside the zeolite. In fact if a bifunctional mechanism of isomerization is involved, then the proximity of Pt and acid sites can be responsible for the observed higher isomerization activity.

4. Conclusions

The main conclusions of this work can be summarized as follows:

- HY zeolites can be effective catalysts for the ring contraction and one-ring opening of decalin, but the density of acid sites needs to be adjusted to an intermediate optimum, high enough to achieve conversion, but not too high that would result in fast deactivation.
- From the conversion of decalin, RO products can be obtained as secondary products via cracking of RC intermediates.
- The low *cis*-to-*trans* ratios obtained in the products are due both to the *cis*-to-*trans* isomerization, but more importantly, to a much higher reactivity of *cis*-decalin than *trans*-decalin. Also, *cis*-decalin converts much more selectively to RO products than *trans*-decalin.
- The production of RC and RO products from tetralin is greatly enhanced in the presence of Pt due to hydrogenation of tetralin to decalin. In the presence of hydrogen Pt/HY catalysts as well as physical mixtures of HY and Pt are much more effective than HY catalysts.

Acknowledgments

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