

Ring contraction and selective ring opening of naphthenic molecules for octane number improvement

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Abstract

Different catalytic strategies have been evaluated to maximize the production of non-aromatic compounds with high octane number, starting from naphthenic molecules, which are typically obtained from the saturation of aromatics. The research octane number (RON), the motor octane number (MON), and the specific volume of the product mixtures were evaluated in each case. The product distribution obtained on acidic and Pt-containing zeolites was investigated in the temperature range 533–563 K in the presence of hydrogen at a total pressure of 2 MPa. It was found that skeletal isomerization (ring contraction) was the primary reaction in both HY and Pt/HY catalysts. The presence of Pt was found to enhance the stability of the catalyst, but also greatly altered the distribution of RC products, enhancing 1,1-dimethylcyclopentane. This enhancement can be explained in terms of a higher rate of hydride transfer caused by the presence of the metal. Evaluation of the octane numbers of the product indicated that a mixture of RC products results in rather high RON, but the MON and specific volume were about the same as that of the feed. To improve MON and specific volume an Ir/SiO₂ catalyst with high hydrogenolysis activity was added to realize the ring opening (RO). The combination of RC and RO was tested on physical mixtures and segregated beds of Pt/HY and Ir/SiO₂ catalysts in order to optimize the production of the iso-alkanes with highest octane number. It was found that with segregated catalyst beds, a better control of the selective breaking of C–C bonds of RC isomers can be achieved, which optimizes octane number and specific volume.

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Keywords: Methylcyclohexane; Ring opening; Ring contraction; Cracking; Gasoline; Octane number; RON; MON; Pt; HY zeolite; Ir/SiO₂

1. Introduction

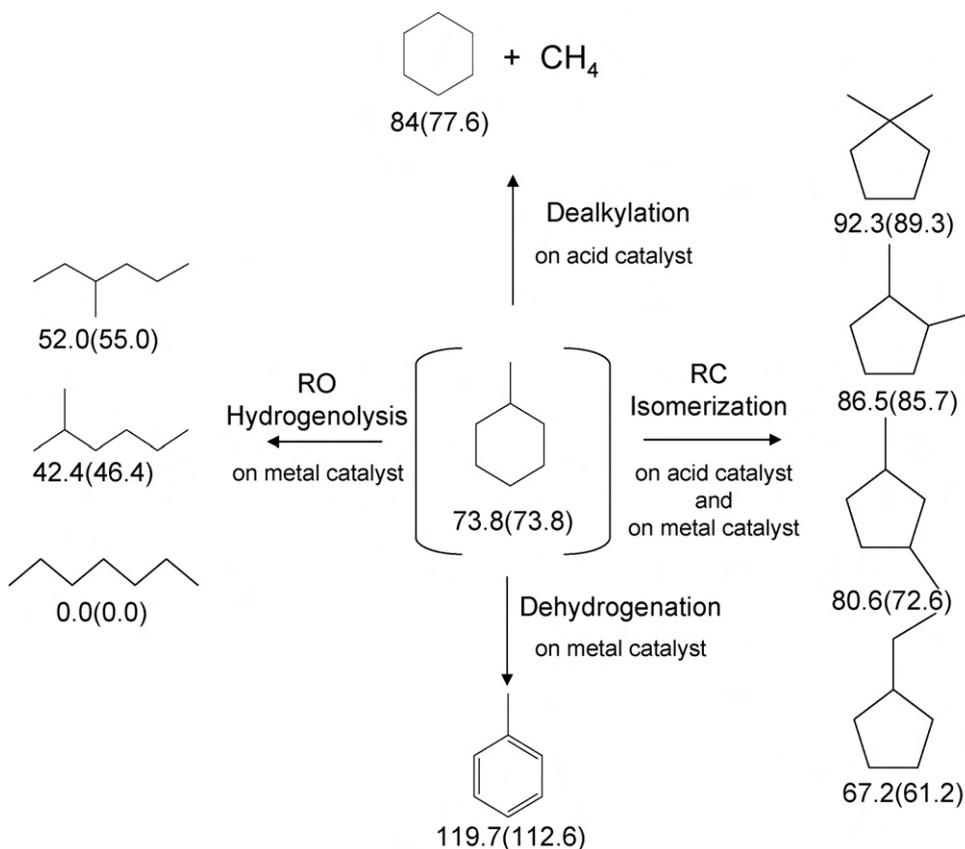
Environmental regulations set limits in the content of aromatics in motor gasolines and impose a challenge to refiners, who need to maintain high octane numbers while decreasing aromatic content [1–3]. Hydrogenation of aromatics into alkylcyclohexanes (naphthenes) would result in significant losses of octane number [4–6] and hydrocracking would lead to losses in molecular weight with consequent losses, in gasoline yield [7,8]. An interesting aspect to investigate is the conversion of naphthenes into non-aromatic compounds with the same number of carbon atoms as the original molecule, but with higher octane number. Octane number provides an indication of the ability of a gasoline to resist knocking as it burns in the engine. There are two test methods to measure the octane

number of a gasoline. These methods use different engine conditions, mainly the intake temperature and the engine speed. The research octane number (RON) method represents engine operations typical of mild driving, without consistent heavy loads on the engine, while the motor octane number (MON) method represents severe, sustained high speed, high load driving. The pump octane number is the average between the two methods (RON + MON)/2. For most gasoline fuels, RON is higher than MON. The difference between the two (RON–MON) is called Sensitivity. Modern fuels are expected to have low sensitivities. Therefore, refiners are concerned about keeping both high RON and high MON.

The conversion of naphthenic molecules has been extensively investigated on metal, acidic, and bifunctional (metal/acid) catalysts for many years. Several reactions are known to occur, such as isomerization (including ring contraction), ring opening, dehydrogenation, and cracking, depending mainly on the reaction conditions, the feed, and the catalysts used [9]. Methylcyclohexane (MCH) is an interesting probe molecule

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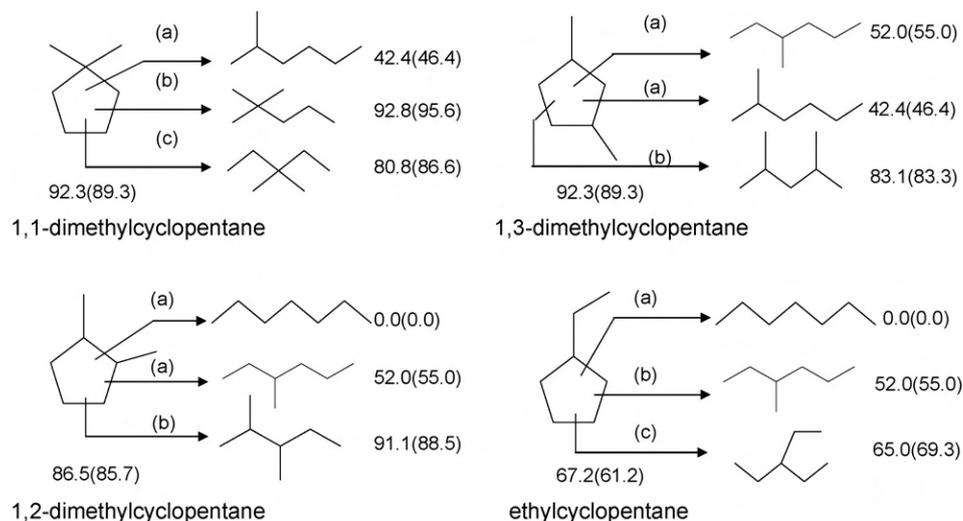
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Scheme 1. Possible products from methylcyclohexane and their research octane number (RON) and their motor octane number (MON).

that can undergo all of the reactions mentioned above and can be used as a model feed. Therefore, it is interesting to compare the octane number of each of the different products that can result in the reactions that MCH can undergo and determine which catalyst or combination of catalysts and reaction conditions can be used to maximize octane numbers (both RON and MON).

As illustrated in [Scheme 1](#), a direct ring opening (RO) of the C₆-ring is not desirable because all of the resulting RO products have low octane number. By contrast, some ring-contraction (RC) products (dimethylcyclopentanes DMCPs) and some secondary ring opening products of the DMCPs (see [Scheme 2](#)) have relatively high octane number and would be a desirable product in gasoline.



Scheme 2. Hydrogenolysis on metal catalysts: product from ring opening reactions of C₇ ring-contraction compounds and their corresponding research octane number and motor octane number.

In general, the RC products have higher RON, while the RO products tend to have higher MON. In this contribution, we analyze different catalysts and catalyst bed configurations to maximize those products of high octane number. We have quantified the effectiveness of different reaction strategies to maximize RON, MON, and gasoline volume.

Previous researchers have studied the reaction paths and the role of catalyst structure on product distribution for MCH reaction. For example, Mignard et al. [10] have studied the conversion of MCH on Pt/USY catalysts. They found that MCH is first isomerized via ring contraction (RC) into ethylcyclopentane (ECP) and dimethylcyclopentanes (DMCPs) and then transformed into C₇ iso-alkanes and cracking (<C₇) products, respectively, as the reaction temperature increases. In that study the individual RC products were lumped, but as shown in Scheme 1, different RC products have very different ON. The intermediate RC step has been made evident in several other studies on acidic catalysts, both zeolitic and non-zeolitic [11]. In some cases, the RC reaction has been proposed to occur by a bifunctional path, involving dehydrogenation on metals. For example, Belatel et al. [12] investigated the MCH reaction on Pt-Ir/sulfated zirconia catalysts and showed that no isomerization was found to take place in the absence of metals.

On zeolitic catalysts, the structure of the zeolite can be used to greatly modify the product distribution. The role of shape selectivity in determining the product distribution of isomerization of naphthenic rings was pointed out by Weitkamp et al. [13] in their work on Pt/HZSM-5 catalysts. They found that on these small-pore catalysts, no 1,1- or 1,2-dimethylcyclopentane were formed while *cis/trans*-1,3-dimethylcyclopentane appeared even at very low conversions. These results are very relevant to understand some of the findings of the present investigation and will be further discussed.

The role of metals is not only the dehydrogenation/hydrogenation steps. It may also participate in ring opening of naphthenic molecules. The principal path for ring opening on catalysts with only the metal function is hydrogenolysis. In this reaction, the cleavage of a C–C bond of alkylcycloalkanes depends on the nature of the catalyst, the type of ring, and the presence of alkyl substituents. Gault [14] identified three different paths for ring opening via hydrogenolysis. The most common pathway involves a dicarbene intermediate with cleavage at the unsubstituted secondary–secondary C–C bond. In the other two reaction paths the cleavage occurs at substituted C–C bonds through π -adsorbed olefin and metallocyclobutane intermediates, respectively. The product distribution from the hydrogenolytic ring opening over metals (i.e. Pt, Ir, Rh and Ru) is strongly dependent on the nature of reactants and catalyst structure, which in turn can be modified by parameters, such as particle size or metal–support interactions [15]. For example, the products obtained from ring opening of methylcyclopentane on high loading, low dispersion Pt/Al₂O₃ catalysts were mostly 2-methylpentane (2-MP) and 3-methylpentane (3-MP) with no *n*-hexane (*n*-Hx). The first two products result from a dicarbene intermediate, the third one requires cleavage of a substituted C–C bond. By contrast, significant amounts of *n*-Hx were found in the

products when the catalyst was a highly dispersed, low loading Pt/Al₂O₃. In contrast to Pt, the behavior of Ir was found to be much less sensitive to catalyst particle size [16–18]. McVicker et al. [17] have investigated that the ring opening of alkylcyclohexanes on iridium (Ir) metal is mainly via a dicarbene mechanism. Also, Weisang and Gault [18] observed that hydrogenolysis of MCP on Ir only yields 2-methylpentane and 3-methylpentane. More recently, our group has found that the dicarbene path is dominant when Ir is supported on silica. However, when the support is alumina, the contribution of products arising from the cleavage of substituted C–C bonds becomes important [19].

In the present contribution, experiments were conducted on acidic and bifunctional catalysts (HY and Pt/HY zeolites, respectively) as well as on metal catalysts of high hydrogenolysis activity (Ir/SiO₂). We have chosen Ir/SiO₂ because, as shown before [19], this catalyst preferentially opens C–C bonds via dicarbene intermediates involving secondary–secondary carbons (illustrated by cleavage at positions (b) and (c) in Scheme 2). As shown in Scheme 2, this type of cleavage results in higher ON. Also, to study the combination of RC and RO reactions, several experiments were conducted on consecutive catalyst beds of Pt/HY and Ir/SiO₂ at different reaction temperatures.

2. Experimental

2.1. Catalyst preparation

The HY zeolite was prepared by ion-exchange of a NaY zeolite (Y54 from UOP, Si/Al = 5.3). Four successive exchanges were conducted with an aqueous solution containing 120.5 g ammonium chloride dissolved in a liter of deionized water with 100 g of NaY. Each suspension was refluxed and stirred with a magnetic plate for 2 h. The solid was then filtered and washed with deionized water. After each ion-exchange step, the sample was filtered and washed. In the final step, the sample was thoroughly washed with deionized water until it was chloride-free. The solid was finally dried in air at 383 K and kept in a desiccator. Before using, the samples were calcined in flow of air at 773 K for 2 h at the heating rate of 0.5 K/min. The Pt/HY and Ir/SiO₂ catalysts were prepared by incipient wetness impregnation of the HY and silica (Hisil-210 from PPG) supports with hexachloroplatinic acid (from Acros) and iridium chloride (from AlfaAesar), respectively. In both cases, the nominal metal content was 1 wt.%. After impregnation, the catalysts were dried at 383 K overnight and then calcined in oxygen at 573 K for 3 h. Prior to the activity measurements, the catalysts were reduced in situ in flow of hydrogen at 673 K for 2 h.

2.2. Catalyst characterization

2.2.1. Temperature programmed desorption (TPD) of adsorbed ammonia

The acidity densities of the HY and Pt/HY catalysts were determined by TPD of adsorbed ammonia. The tests were

conducted in a 1/4" 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 to room temperature under He flow; at which point, 2% NH₃/He was passed over the sample in an amount that greatly exceeds the total number of acid sites to assure saturation of all 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 in flow of He 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 desorbed was determined by a calibration curve obtained by varying volumes of 2% NH₃/He.

2.2.2. Hydrogen chemisorption

Pt and Ir dispersions were estimated from volumetric H₂ chemisorption uptake measurements at 300 K in a chemisorption apparatus. Before each measurement, the catalysts were treated in H₂ at 673 K for 2 h and then evacuated for 0.5 h at 673 K. After the treatment at 673 K, the samples were cooled at 300 K and H₂ chemisorption uptakes were measured in the 1–80 Torr pressure range. After evacuation at room temperature, a second H₂ isotherm was performed to obtain an estimate of the reversible and irreversible uptakes. The irreversible H/M ratios were determined from the difference between the two isotherms.

2.2.3. Transmission electron microscopy (TEM)

A JOEL JSM-2000FX high-resolution analytical electron microscope equipped with a field emission cathode operated at 200 keV was used to visualize the dispersion of the metal particles on the samples. For this analysis, the catalyst samples treated ex situ were first dispersed by ultrasonication in isopropanol for 15 min, then dropped on holey carbon coated copper grids and dried before analysis.

2.2.4. Catalytic activity testing

The methylcyclohexane reaction (MCH, Aldrich, >99%) was conducted in a 3/8" stainless steel reactor equipped with a thermowell with a thermocouple placed in the center of the bed. Prior to each experiment, the specified amount of catalyst was diluted with inert alumina to make a volume of catalyst bed of 2 ml and placed in the center of the reactor. The top and the bottom part of the catalyst bed were filled with glass beads of 1 mm in a diameter, to ensure an effective preheating and

minimize heat losses. Before starting the feed of MCH from a high-pressure liquid pump through a vaporizer, the catalysts were reduced in situ at 673 K for 2 h in flow of pure hydrogen. The catalytic activity was measured in the temperature range 513–593 K, at a total pressure of 2 MPa and at a H₂/MCH molar ratio of 40. The space velocities were systematically varied by changing either the catalyst amount or the feed rate. The production of light products and gases (<C₇) was very low in most runs. These products are lumped as "cracking products" in Tables 2–4. While the liquids yields were not determined for every run, they were greater than (100-cracking yield).

In addition to the runs on individual catalysts, a set of experiments was conducted with physical mixtures of Pt/HY and Ir/SiO₂ catalysts. In two of these experiments, the two catalysts were segregated in separate beds with the Pt/HY catalyst placed in the front end and the Ir/SiO₂ catalyst in the back. In the system identified as Pt/HY > Ir/SiO₂, both catalysts were kept at the same temperature. By contrast, in the system identified as Pt/HY ≫ Ir/SiO₂, the Pt/HY catalyst was kept at 20 K higher temperature than the Ir/SiO₂ catalyst. In the third experiment, the Pt/HY and Ir/SiO₂ catalysts were well mixed in a weight ratio of 2:1, respectively. In all runs, the products were analyzed online in a HP5890 gas chromatograph with FID detector.

3. Results and discussion

3.1. Catalyst characterization

The main properties of the HY zeolite, Pt/HY and Ir/SiO₂ catalysts are summarized in Table 1. It is clear that the bare HY zeolite contains a larger amount of acid sites than that impregnated with Pt. As previously observed [20] the impregnation with Pt results in a loss of acid sites (~300 μmol/g) that significantly exceeds the number of moles of metal incorporated (50 μmol/g), which may indicate some pore blocking during the Pt impregnation process.

The H₂ uptakes of H/Pt = 2.0 and H/Ir = 2.3 for the Pt/HY and Ir/SiO₂ catalysts, respectively, indicate a high metal dispersion in both cases. H/M ratios higher than one have been previously reported [21–23]. Representative TEM images for Pt/HY and Ir/SiO₂ catalysts are shown in Fig. 1. The images reveal that the metal particles in both catalysts were uniformly dispersed on the supports with a fraction of the particles ranging

Table 1
Characterization of fresh catalysts

Sample	Metal loading (wt.%)	H/M experiments		Total acidity ^a Amount of desorbed NH ₃ (μmol/g cat.)	Acidity ^b (μmol Py/g cat.)					
		V(H ₂) (cm ³ /g cat.)	H/M		Brönsted (1545 cm ⁻¹)			Lewis (1445 cm ⁻¹)		
					523 K	623 K	673 K	523 K	623 K	673 K
HY	–	–	–	1109	352	328	324	666	523	76
Pt/HY	1.0	1.2	2.0	795	311	295	273	551	512	140
Ir/SiO ₂	1.0	1.4	2.3	–	–	–	–	–	–	–

^a Total acidity measured by TPD of NH₃.

^b Acidity measured by adsorbed pyridine at different temperatures. Catalysts were reduced at 673 K for 2 h under H₂ flow.

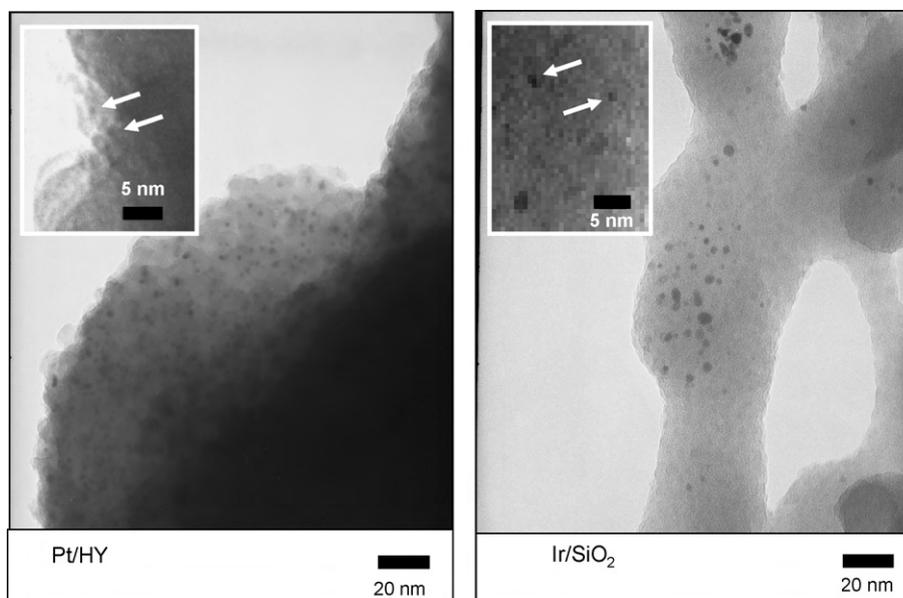


Fig. 1. TEM images of the Pt/HY and Ir/SiO₂ samples. The length of the bar is 20 nm in the micrographs and 5 nm in the insets.

in the size 5–10 nm and another fraction below 1 nm, in agreement with the high hydrogen uptakes.

3.2. Conversion of methylcyclohexane over HY and Pt/HY catalysts

The product distribution and level of MCH conversion obtained over an acidic HY catalyst and a bifunctional Pt/HY catalyst are compared in Table 2 for two different times on stream, 1 and 6 h. Significant differences in initial activity, rate of deactivation, and product distribution are observed between the two catalysts. While other effects might be present, it is likely that the higher initial activity of the HY catalyst could be attributed to the higher density of acid sites present on the bare HY zeolite. A drastic decay in activity as a function of time on stream was observed for the HY catalyst (51.3% conversion after 1 h, 32.3% after 6 h). The fast deactivation was accompanied by a pronounced decrease in the concentration of cracking products (<C₇), which went from 13.5 wt.% during the first hour on stream to 2.3 wt.% after 6 h. In contrast, almost no deactivation was evident on the Pt/HY catalyst, for which the total conversion remained practically constant (~29%) over the time of the study. The higher resistance to deactivation exhibited by the Pt-containing catalyst may be attributed to a higher rate of hydrogen transfer accelerated by the presence of the metal and the high H₂/hydrocarbon ratio used in this study.

A significant difference between HY and Pt/HY catalysts was also observed in the product distribution. Similar to the reaction of most naphthenes [9], in the conversion of MCH the ring contraction is the primary reaction; subsequently, the RC products are consumed by consecutive reactions that first produce RO products and then cracking products (<C₇). A clear demonstration of this sequence of reactions is obtained by plotting the evolution of products as a function of conversion, as discussed below.

On the HY catalyst, while equilibrium is not reached, the distribution of RC products are more or less in line with their thermodynamic stability; that is, *trans*-1,2 dimethylcyclopentane (*trans*-1,2 DMCP) is the most abundant product, followed by *cis*- and *trans*-1,3 DMCP. These three products are desirable

Table 2

Product distributions of methylcyclohexane reaction on acidic HY and bifunctional Pt/HY catalysts at different times on stream

Catalysts Space time; W/F (h)	HY 0.49		Pt/HY 0.47		
	1	6	1	6	
Conversion (%)	51.3	32.3	29.9	29.2	
MCH (wt.%)	48.7	67.7	70.1	70.8	
RC/RO ratio	10.1	38.2	40.9	46.6	
Products	Selectivity to (%)				
Cracking products	26.3	7.2	0.3	0.2	
RC products	(RON)	Selectivity to (%)			
1,1-DMCP	(92.3)	2.6	1.3	13.3	13.1
<i>cis</i> -1,3-DMCP	(79.2)	16.7	24.8	16.0	15.9
<i>trans</i> -1,3-DMCP	(80.6)	16.2	23.3	15.8	15.6
<i>trans</i> -1,2-DMCP	(86.5)	20.7	25.2	26.0	26.0
ECP	(67.2)	10.0	15.7	26.2	27.0
RO products	(RON)	Selectivity to (%)			
3,3-DMP	(80.8)	–	–	–	–
2,2-DMP	(92.8)	–	–	0.2	0.1
2,4-DMP	(83.1)	5.7	2.1	0.6	0.5
2,3-DMP	(91.1)	0.2	–	0.2	0.2
<i>n</i> -Heptane	(0.0)	–	–	0.7	0.6
2-MH	(42.4)	0.6	0.2	0.7	0.6
3-MH	(52.0)	–	–	–	–
3-EP	(65.0)	–	–	–	–
Heavy products		1.0	–	–	–

Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H₂/MCH molar ratio = 40.

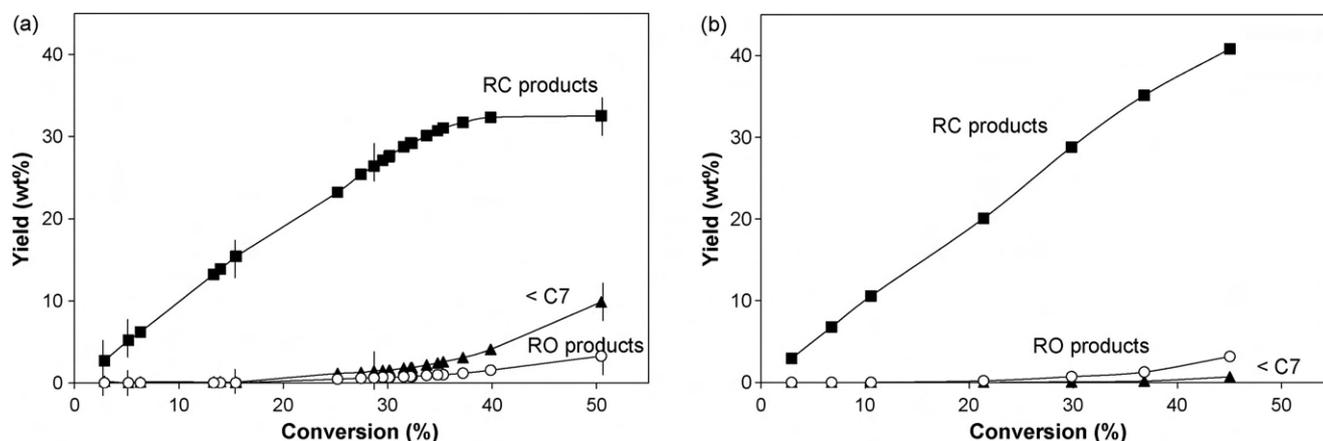


Fig. 2. (a) Product distribution of methylcyclohexane reaction over HY as a function of conversion. Conversions were varied by space times and time on stream. Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H_2/MCH molar ratio = 40. (b) Product distribution of methylcyclohexane reaction over Pt/HY as a function of conversion. Conversions were varied by changing space time. Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H_2/MCH molar ratio = 40.

since they have relatively high octane number. Unfortunately, together with these products, ethylcyclopentane (ECP), which has a very low octane number, is produced in large concentrations. As shown in Scheme 2, opening the ECP ring would not enhance the octane number either, since every RO product from ECP has an octane number that is even lower than that of ECP. Interestingly, some RO products are observed on the HY catalyst, and the most abundant product is 2,4-dimethylpentane (2,4-DMP), which is obtained by β -scission of 1,3-dimethylcyclopentane (1,3-DMCP). One may have expected a comparable amount of 2,3-DMP, which could be produced by an analogous β -scission of 1,2-DMCP and has a high octane number. However, this product is only produced in small quantities.

The product distribution obtained on the Pt/HY catalyst was significantly different from that on the HY catalyst. The most obvious difference was the drastic decrease in cracking products, which can be ascribed to both lower acidity and enhanced hydrogen transfer by the presence of Pt. The latter is most probably the dominant effect, which results in reduced lifetime of the carbonium ion intermediates on surfaces. At the same time, the distribution of DMCP products is significantly altered. It is seen that, at a given conversion the yield of 1,1-DMCP and ECP is greatly enhanced when Pt is present.

3.3. Evolution of product distribution with conversion

The yields of the different products obtained over HY and Pt/HY as a function of total conversion are compared in Fig. 2(a and b). It is observed, that at low conversions, only the RC products are found on both catalysts, while as the conversion increases, RO and cracking products start to appear. This trend clearly shows that the RC isomerization of MCH to ECP and DMCPs is a primary reaction. The secondary ring opening products consist mostly of 2,4-DMP, 2-MH, and *n*-heptane, but they further react yielding cracking products, a trend that is particularly apparent on the HY catalyst.

Fig. 3 shows some differences in the distribution of the RC products for HY and Pt/HY catalysts. It can be seen that the selectivity to the low octane number, monobranched isomer (ECP) decreases with conversion, while that to the dibranched isomers (DMCPs) increases. This is a favorable selectivity change because it should result in an increase in octane number. This trend may be explained considering that at low conversions ECP is easily formed via an internal alkyl shifts, called type-A isomerization in previous studies [24]. The increase in the selectivity to the thermodynamically favored DMCP isomers observed at higher space times may be due to a stepwise isomerization [10] as that observed in the isomerization of ethylcyclohexane on Pt/HZSM-5 [25], which produces propylcyclopentane as a main primary product, followed by formation of dibranched isomers as secondary products. In contrast to this proposed sequence, Calemma et al. [26] have shown that both ECP and DMCPs are primary products from the MCH reaction over Pt/H-mordenite. In fact, the extrapolation to zero conversion in Fig. 3 indicates that it is possible that

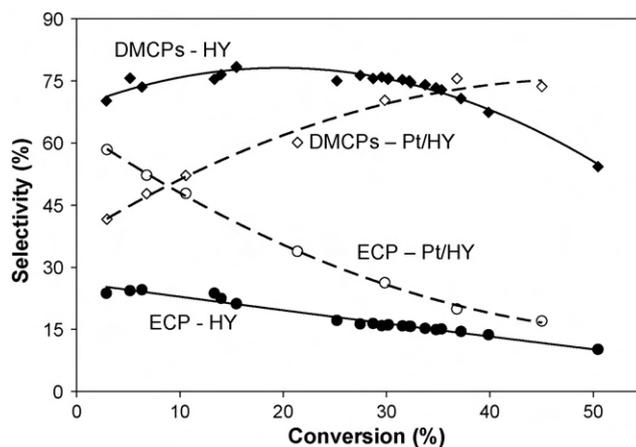


Fig. 3. Isomerized RC products of methylcyclohexane reaction over HY (solid symbols) and Pt/HY (open symbols) at varying conversion. Conversions were varied by space time and time on stream. Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H_2/MCH molar ratio = 40.

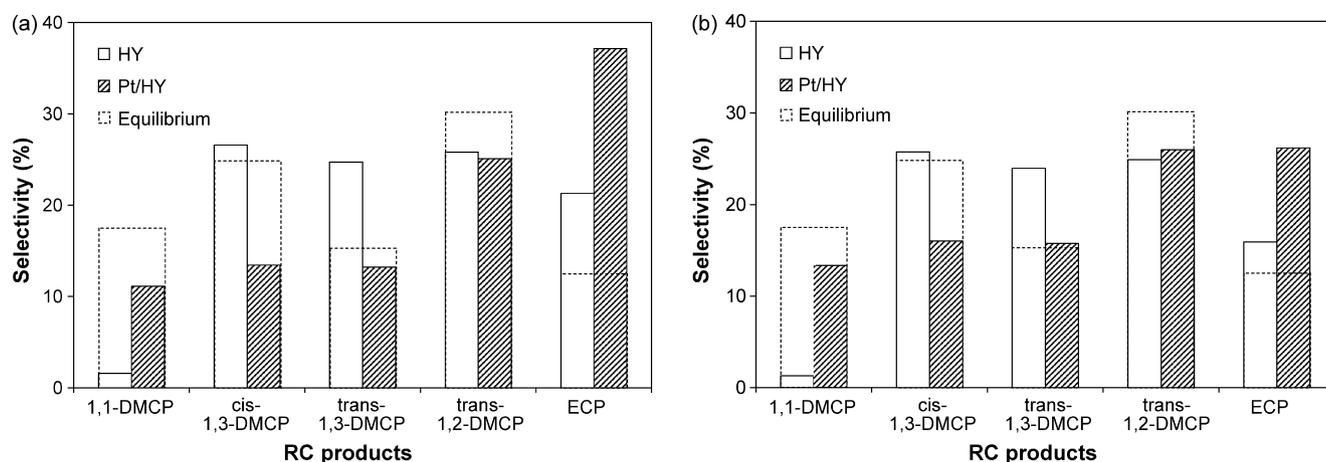


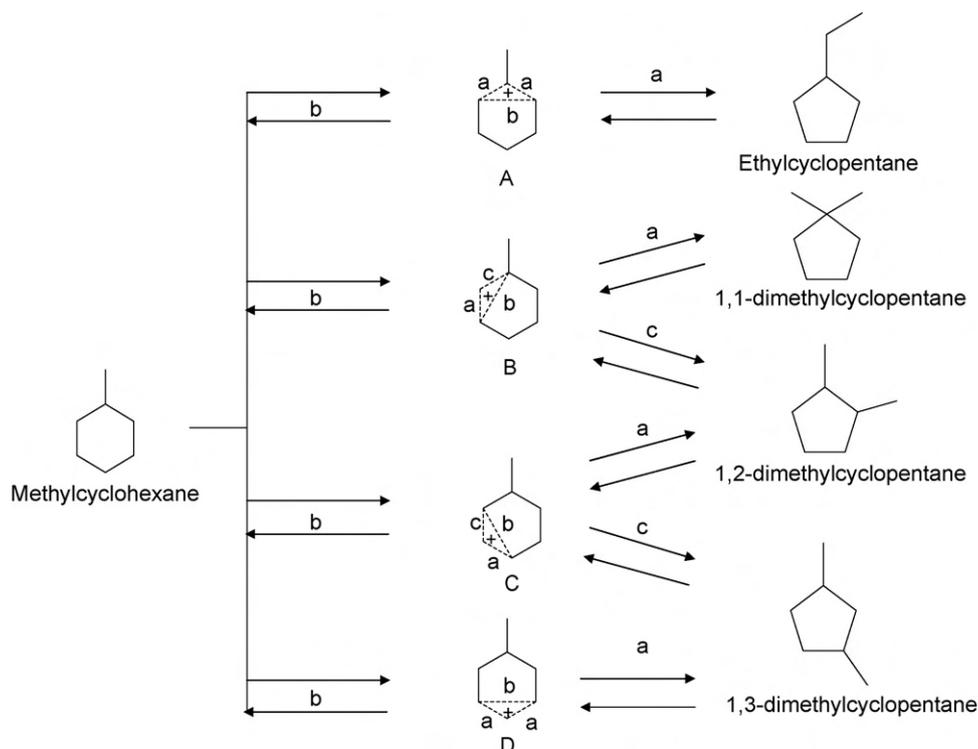
Fig. 4. (a) Selectivities of isomerized RC products on HY and Pt/HY at the same conversion ($\sim 16\%$). Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H_2/MCH molar ratio = 40. (b) Selectivities to isomerized RC products on HY and Pt/HY at the same conversion ($\sim 30\%$). Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Reaction conditions: total pressure = 2 MPa; temperature = 533 K; H_2/MCH molar ratio = 40.

some DMCPs are produced as primary products at low space times and low conversions. However, they are also formed by secondary reaction at higher conversions.

More detailed information on the distribution of RC products over HY and Pt/HY catalysts at two different total MCH conversions (~ 16 and $\sim 30\%$) are shown in Fig. 4(a and b), together with the simulated composition of RC products in equilibrium. It must be noted that in both, the selectivity and equilibrium calculations only the RC products were considered. These figures clearly illustrate the characteristic differences between HY and Pt/HY; that is, for a given conversion, the selectivities to ECP and 1,1-DMCP are lower on HY than on Pt/

HY while the selectivity to 1,3-DMCP is higher. The difference is particularly important for the selectivity towards the most desirable isomer 1,1-DMCP (high octane number), which is significant for Pt/HY but very low on HY at both conversion levels.

The enhanced selectivity to ECP on the Pt/HY, particularly at low conversions, is consistent with both, a lower acidity density [11] and an enhanced rate of hydrogen transfer in this catalyst compared to HY [27]. The capacity of Pt for activating hydrogen and accelerating the hydride transfer step has been well documented in literature [28–30]. According to concepts previously proposed, an enhanced rate of hydride transfer



Scheme 3. Carbocation chemistry for the ring-contraction reactions.

Table 3
Product distribution of methylcyclohexane reaction over Pt/HY at different temperatures and varying space time

Catalyst		Pt/HY W/F = 0.6 h				Pt/HY W/F = 0.8 h				Equilibrium ^a	
Temperature (K)	513	533	553	553	533	553	593	533	553		
Conversion (%)	13.2	31.6	48.4	58.9	38.2	50.9	70.3	49.5	54.3		
MCH (wt.%)	86.8	68.4	51.6	41.1	61.8	49.1	29.7	50.5	46.6		
Products		Yield (wt.%)				Yield (wt.%)				Yield (wt.%)	
Cracking products	(RON)	0.4	0.5	0.8	2.3	0.4	1.4	13.5	–	–	
1,1-DMCP	(92.3)	1.2	4.3	7.2	9.0	5.5	7.5	9.4	8.0	8.4	
<i>cis</i> -1,3-DMCP	(79.2)	1.3	5.2	9.4	11.1	6.9	9.7	9.4	11.7	12.5	
<i>trans</i> -1,3-DMCP	(80.6)	1.2	5.1	9.3	11.1	6.8	9.6	9.7	7.0	7.7	
<i>cis</i> -1,2-DMCP	(85.7)	–	–	–	–	–	–	–	2.6	3.0	
<i>trans</i> -1,2-DMCP	(86.5)	3.1	8.3	12.9	14.5	10.1	13.2	12.2	14.2	15.1	
ECP	(67.2)	5.9	7.7	7.2	6.7	7.5	7.3	6.1	5.9	6.7	
3,3-DMP	(80.8)	–	–	0.1	0.2	–	0.1	0.5	–	–	
2,2-DMP	(92.8)	–	–	0.1	0.3	0.1	0.2	0.7	–	–	
2,4-DMP	(83.1)	–	0.1	0.4	1.0	0.3	0.6	2.6	–	–	
2,3-DMP	(91.1)	–	–	0.1	0.4	0.1	0.2	1.0	–	–	
<i>n</i> -Heptane	(0.0)	0.1	0.1	0.3	0.7	0.2	0.4	1.8	–	–	
2-MH	(42.4)	–	0.1	0.4	1.3	0.3	0.7	2.9	–	–	
3-MH	(52.0)	–	–	–	–	–	–	–	–	–	
3-EP	(65.0)	–	–	–	–	–	–	–	–	–	

Reaction conditions: total pressure = 2 MPa, H₂/MCH molar ratio = 40.

^a Simulated RC isomers composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION.

accelerates the rate of desorption and thus reduces the residence time of intermediates on the surface. Since ECP is the product resulting from the C6-ring surface carbocation that is the easiest to form (intermediate A in Scheme 3), shortening the residence time of this surface intermediate will increase the concentration of ECP in the products. By contrast, on the HY catalyst, the carbocation has more time on the surface to isomerize and, as a result, the 1,3-DMCP and 1,2-DMCP are formed via the least favored intermediates B, C, and D.

Similarly, the enhanced selectivity to 1,1-DMCP on Pt/HY is also consistent with an enhanced rate of hydride transfer. However, in this case, the fate of the C5-ring carbocations needs to be addressed. Once the RC step occurs on the surface and the corresponding C5-ring carbocation is formed, the RC product can only be obtained by a hydride transfer step. On the HY catalyst, this step is bimolecular and involves electroneutral RH molecules (e.g. MCH).

The production of 1,1-DMCP involves a 2,2-dimethylcyclopent-1-yl cation. With such a bulky intermediate, the hydride transfer from an electroneutral RH molecule is sterically unfavorable and one can expect this step to be slow. As a result, the production of 1,1-DMCP is very low on an HY catalyst. However, in the presence of Pt the hydride transfer is enhanced and as a result significant amounts of 1,1-DMCP can be obtained. A similar situation was reported by Santiesteban et al. [31] in the isomerization of *n*-hexane on highly acidic WO₃/ZrO₂-based catalysts. These authors found that the 2,2-dimethylbutane isomer was not formed in the absence of Pt, but it was produced in significant amounts when Pt was added to the catalyst. They suggested that the presence of Pt gives rise to a high concentration of atomic hydrogen on the surface, enough to overcome the high kinetic

barrier associated with the intermolecular hydride transfer to the sterically hindered intermediate (i.e. 2,2-dimethyl-3-butyl cation).

The effect of reaction temperature on product distribution is summarized in Table 3 for two different space times (0.6 and 0.8 h). The isomerization products (RC) (primary products) decrease with increasing space time; while the ring opening and cracking products (secondary products) increase. The effect of temperature is further illustrated in Fig. 5(a and b) for a constant W/F = 0.6 h. Below 553 K, the only observed products are RC products, while RO and cracking products only appear at high temperatures. At the lower temperature end, ECP is the dominant product, while at 593 K the equilibrium product distribution is obtained.

Among the RC isomers, only ECP has an octane number (both RON and MON) lower than the feed, but as shown above, ECP is the dominant product only at low conversions. One can evaluate the variation of octane number as a function of conversion in the product mixture. However, it is well known that the RON and MON of a hydrocarbon mixture is not the direct linear combination of the individual contributions, but rather they vary in a non-linear form Ref. [34].

Ghosh et al. [32] have recently recommended the use of a model for the prediction of RON and MON in gasoline blends. They have confirmed that the model can accurately predict RON and MON, within 1 number. This model takes into account the interactions among the different hydrocarbon classes (paraffins, olefins, aromatics, etc.) in a gasoline blend that are responsible for the non-linear behavior of octane numbers. The advantage of this equation is that it does not use blending numbers, but rather the individual ON of the pure components, that are readily available [33,34].

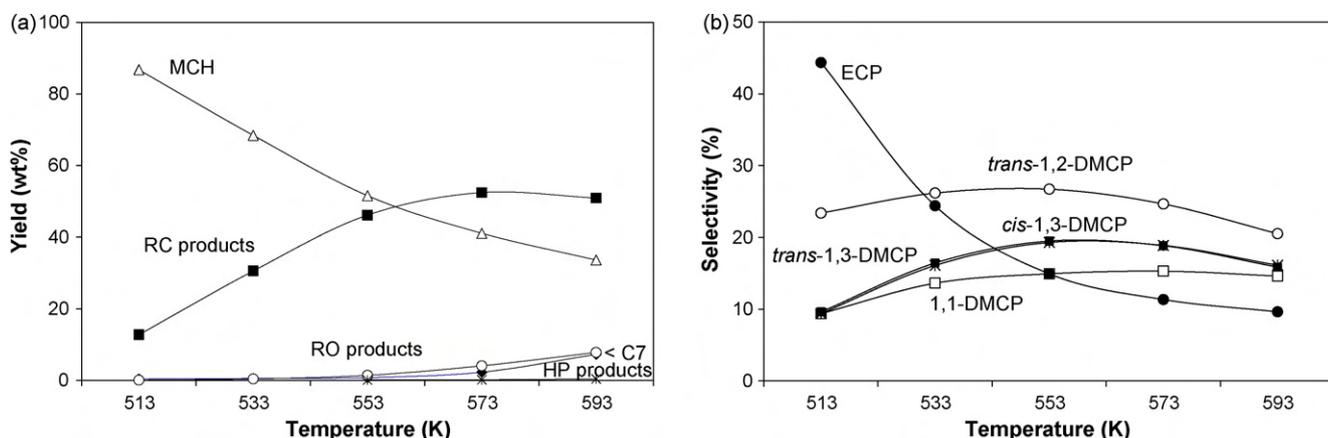


Fig. 5. (a) Product distributions of methylcyclohexane reaction over Pt/HY at different reaction temperatures. Reaction conditions: total pressure = 2 MPa; $W/F = 0.6$ h; H_2/MCH molar ratio = 40. (b) Selectivities to ring-contraction products at different reaction temperatures. Reaction conditions: total pressure = 2 MPa; $W/F = 0.6$ h; H_2/MCH molar ratio = 40.

Following this ON prediction method, we calculated octane numbers (both RON and MON) for the product mixtures obtained in this work. The results for the products obtained over the HY and Pt/HY catalysts, as well as the equilibrium composition for MCH and all the RC products are presented in Fig. 6(a and b), for RON and MON, respectively. It is observed that the RON of the product mixture on both HY and Pt/HY catalysts increase as a function of MCH conversion. However, at the higher end of MCH conversion (i.e. high reaction temperatures), RON sharply decreases due to the contribution of the ring opening reactions mentioned above that produce low RON molecules. When only RC is considered in the calculation of equilibrium the increase in RON is higher. However, an interesting point to address is that only RON increases as the MCH conversion increases; by contrast MON does not increase, but rather it decreases as MCH is converted into RC isomers.

When analyzing the RON and particularly the MON of some of the RO products in Scheme 2, one can see that selective C–C bond cleavage might lead to isoparaffins of high octane number.

We have attempted to investigate different catalysts and catalytic bed configurations that might result in octane numbers higher than those obtained by ring contraction alone. As previously proposed by McVicker et al. [17], iridium is a promising catalytic material for selective ring opening. As described below, we have investigated using Ir/SiO₂ catalysts in combination with Pt/HY.

3.4. Conversion of methylcyclohexane over Ir/SiO₂

Fig. 7 shows the different products obtained when MCH is reacted over the Ir/SiO₂ catalyst at different temperatures. It is clear that, on this catalyst, the only reaction observed under these conditions is the direct ring opening of the C₆-ring of MCH into C₇-alkanes (i.e. 2-MH, 3-MH, and *n*-heptane). In contrast to the other two catalysts, no RC products were observed on Ir/SiO₂, clearly showing that the RC is catalyzed by acids [11,12]. Monofunctional isomerization has been previously observed on Ir catalysts, but under the conditions of this study, hydrogenolysis is dominant. As first reported by

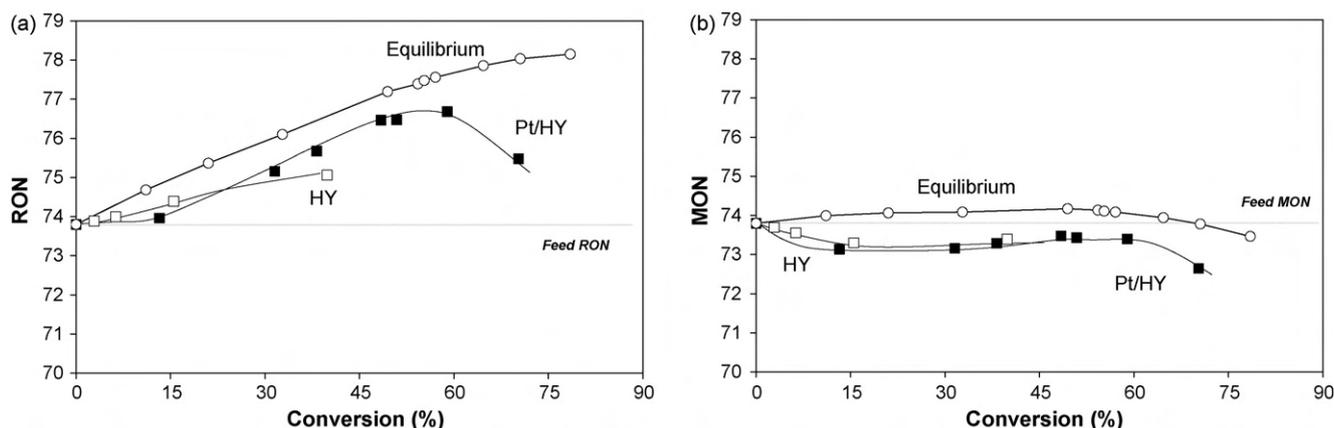


Fig. 6. (a) RON of the product mixture as a function of MCH conversion, calculated by the method of Ref. [32]. Conversion was varied by changing W/F and temperature as shown in Table 3. Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Total pressure = 2 MPa; H_2/MCH molar ratio = 40. (b) MON of the product mixture as a function of MCH conversion, calculated by the method of Ref. [32]. Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Conversion was varied by changing W/F and temperature as shown in Table 3. Total pressure = 2 MPa; H_2/MCH molar ratio = 40.

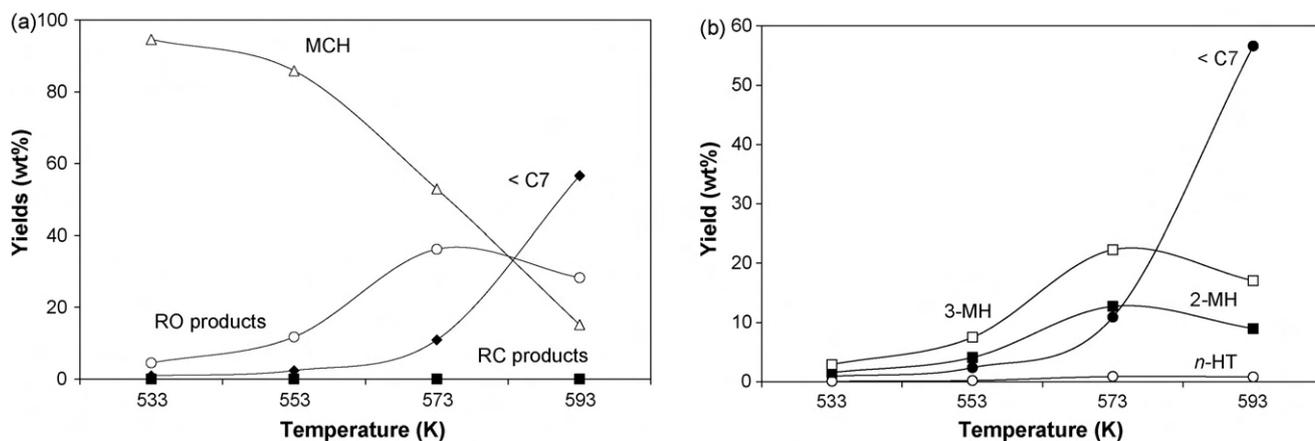


Fig. 7. (a) Product distributions of methylcyclohexane reaction over Ir/SiO₂ at different reaction temperatures. Reaction conditions: total pressure = 2 MPa; $W/F = 0.3$ h; H₂/MCH molar ratio = 40. (b) The distribution of ring opening and cracking products at different reaction temperatures. Reaction conditions: total pressure = 2 MPa; $W/F = 0.3$ h; H₂/MCH molar ratio = 40.

Gault [14] iridium has the tendency of breaking secondary–secondary C–C bonds via dicarbene intermediates while the C–C bond rupture in the vicinity of the tertiary carbon is strongly hindered. This is indeed the behavior observed in this case for the Ir/SiO₂ catalyst. We have previously shown that when the support is alumina, the contribution of products arising from the tertiary–secondary C–C bond cleavage may be greatly increased [19]. In general, as shown in Scheme 1, ring opening at a tertiary–secondary C–C bond produces molecules of lower octane number. Indeed, in this case, the resulting C₇ alkane is *n*-heptane with RON = MON = 0. In fact, all three products obtained from direct opening of MCH have RON/MON lower than the feed. Therefore, in order to be effective, the iridium catalyst must be used in combination with an acidic catalyst that produces RC compounds, which as shown in Scheme 2 may lead to higher octane numbers if opened at the right C–C bond.

3.5. Conversion of methylcyclohexane on physical mixtures and segregated beds of Pt/HY and Ir/SiO₂ catalysts

As shown in Scheme 2, only a few of the RO products have higher RON than the RC products. However, two aspects of RO products may be desirable in comparison to RC products. In the first place, while the MON of C₅ naphthenic molecules is lower

than the corresponding RON, the opposite is true for the isoparaffins. That is, the MONs of RC products are generally higher than the corresponding RONs. Second, the density of isoparaffins is generally lower than that of the corresponding naphthene. As a result, there is a volume gain for refiners when the rings are opened. That is, even when there is no gain in octane number, RO may represent a significant gain in volume.

As illustrated in Fig. 8, the following set experiments were conducted to investigate the combination of RC and RO for a given MCH feed: (a) a homogeneous physical mixture of Pt/HY and Ir/SiO₂ designated as (Pt/HY + Ir/SiO₂); in this case, the temperature of the two catalysts is the same during reaction; (b) a two-bed configuration, where the front bed is Pt/HY and the back bed is Ir/SiO₂; in this configuration, designated as (Pt/HY > Ir/SiO₂), the temperature of the two catalyst beds is kept the same; (c) a two-bed configuration, in which the front bed is Pt/HY and the back bed is Ir/SiO₂, designated as (Pt/HY ≫ Ir/SiO₂); the two beds are separated by quartz wool and glass beads and there is temperature difference of 20 K, with the front bed at a higher temperature. In all three configurations, the total amount of each of the catalyst was kept constant.

The results obtained with the three different system configurations are summarized in Table 4. It can be observed that the total MCH conversion increases with temperature much more rapidly for the physical mixture, case (a) Pt/HY + Ir/SiO₂,

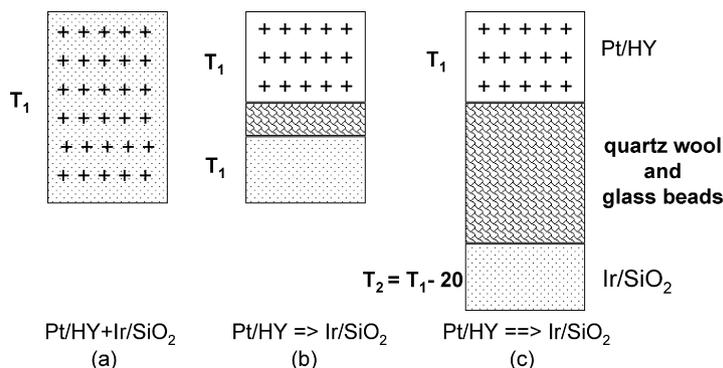


Fig. 8. Schematic reaction system configurations.

Table 4
Product distribution of methylcyclohexane reaction at different reaction system configurations

Catalysts	Pt/HY + Ir/SiO ₂			Pt/HY → Ir/SiO ₂			Pt/HY → Ir/SiO ₂			
	513	533	553	533	553	573	533/513	553/533	573/553	
Temperature (K)	513	533	553	533	553	573	533/513	553/533	573/553	
Conversion (%)	30.1	65.5	90.3	52.6	68.7	92.7	45.8	60.6	67.1	
MCH (wt.%)	69.9	34.5	9.7	47.4	31.3	7.3	54.2	39.4	25.4	
RC products (wt.%)	12.5	12.2	3.1	15.2	4.3	0.4	34.3	20.3	7.3	
RO products (wt.%)	17.0	49.1	76.7	35.0	59.0	66.1	10.6	37.0	54.9	
RC/RO ratio	0.7	0.2	0.0	0.4	0.1	0.0	3.2	0.5	0.1	
Products	Yield (wt.%)			Yield (wt.%)			Yield (wt.%)			
Cracking products	(RON)	0.5	3.9	9.8	2.2	5.2	25.7	0.9	3.1	11.8
1,1-DMCP	(92.3)	0.0	0.0	0.0	0.0	0.0	0.0	7.4	0.0	0.0
<i>cis</i> -1,3-DMCP	(79.2)	1.9	2.3	0.9	3.8	1.8	0.2	6.7	5.4	1.6
<i>trans</i> -1,3-DMCP	(80.6)	2.5	3.4	0.0	5.5	0.0	0.0	7.6	7.2	3.8
<i>trans</i> -1,2-DMCP	(86.5)	3.6	3.5	1.3	4.5	1.9	0.2	8.7	6.0	1.6
ECP	(67.2)	4.5	3.1	1.0	1.5	0.5	0.0	3.9	1.6	0.3
3,3-DMP	(80.8)	0.7	3.4	5.7	0.9	1.5	2.3	0.4	1.1	1.7
2,2-DMP	(92.8)	1.7	6.0	9.1	3.2	5.2	5.7	1.4	3.5	5.2
2,4-DMP	(83.1)	1.9	6.3	8.9	9.7	16.5	14.5	3.5	10.0	15.7
2,3-DMP	(91.1)	2.0	6.7	10.6	9.2	14.5	12.6	4.0	9.9	14.1
<i>n</i> -Heptane	(0.0)	0.4	1.4	3.8	0.9	1.2	2.5	0.4	1.1	2.3
2-MH	(42.4)	2.6	10.1	16.7	2.2	4.5	10.1	0.8	2.3	5.1
3-MH	(52.0)	7.7	15.1	19.5	8.8	11.7	16.5	0.0	9.2	10.8
3-EP	(65.0)	0.0	0.0	2.4	0.0	4.0	1.9	0.0	0.0	0.0

Reaction conditions: total pressure = 2 MPa; *W/F* for Pt/HY = 0.6 h; *W/F* for Ir/SiO₂ = 0.3 h; H₂/MCH molar ratio = 40.

than for the sequential bed configurations. In the physical mixture, a significant amount of C₆-member ring opening takes place, which as mentioned above, is not desirable because it produces compounds of low octane numbers. By contrast, in case (b) (Pt/HY > Ir/SiO₂), a large fraction of MCH is converted to RC products before reaching the Ir/SiO₂ bed. In this case, the opening of C₅-member ring compounds is fast and readily occurs at lower temperatures. As a result, this configuration yields a larger fraction of DMP products, which result from the opening of C₅-member rings. This is a desirable outcome since DMP products have relatively high octane

numbers. However, on this configuration, working at low temperatures results in low MCH conversions, while working at higher temperatures initiates the opening of C₆-member rings, i.e. direct RO of MCH, which produces compounds of low octane numbers. In addition, high reaction temperatures (e.g. 573 K) generate a large fraction of cracking products.

Finally, in the reactor configuration with well-separated catalysts, case (c), we can avoid breaking the C–C bond of MCH by keeping the second bed at a lower temperature. In this way, the C–C bond cleavage of the C₅-member rings, with a lower activation energy [35,36], is less affected by the

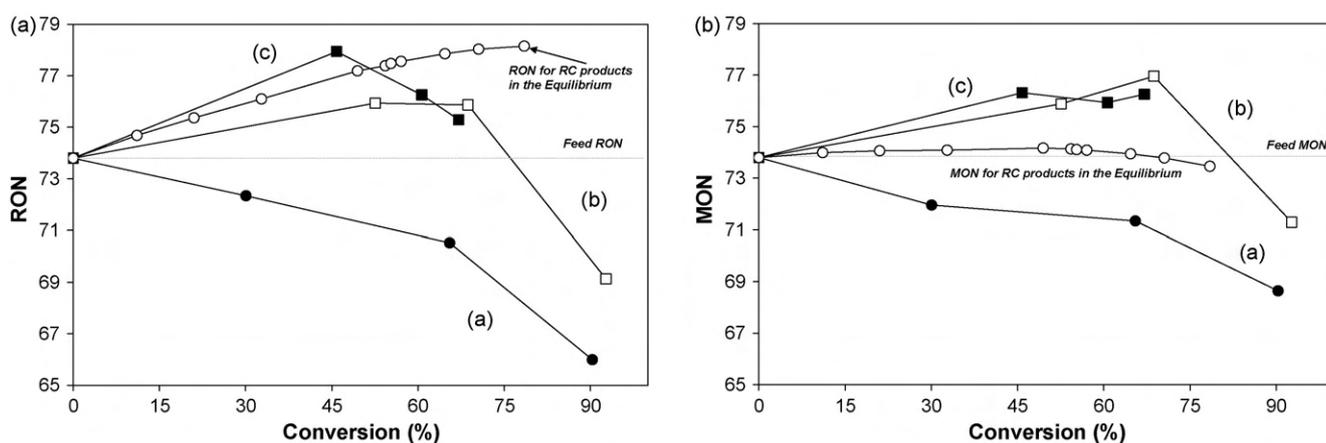


Fig. 9. (a) RON of the product mixture as a function of MCH conversion, calculated by the method of Ref. [32]. For the product distribution obtained on the three Pt/HY + Ir/SiO₂ catalyst bed configurations illustrated in Fig. 8. Conversion was varied by changing temperature as shown in Table 4. Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Total pressure = 2 MPa; H₂/MCH molar ratio = 40. (b) MON of the product mixture as a function of MCH conversion, calculated by the method of Ref. [32]. For the product distribution obtained on the three Pt/HY + Ir/SiO₂ catalyst bed configurations illustrated in Fig. 8. Conversion was varied by changing temperature as shown in Table 4. Simulated RC composition at thermodynamic equilibrium was calculated by using SimSci PRO/II PROVISION. Total pressure = 2 MPa; H₂/MCH molar ratio = 40.

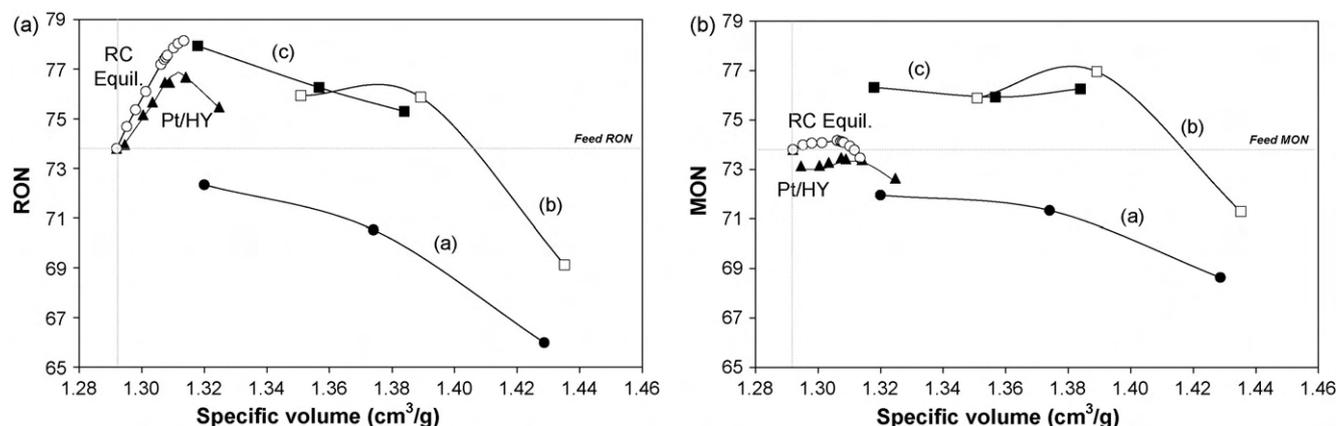


Fig. 10. (a) RON of the product mixture as a function of the corresponding specific volume. The volume was increased by increasing the MCH conversion through RC and by combination of (RC + RO), see Table 4. Curves (a–c) represent the three Pt/HY + Ir/SiO₂ catalyst bed configurations illustrated in Fig. 8. Simulated RC composition at thermodynamic equilibrium as well as the specific volume of mixtures were calculated by using SimSci PRO/II PROVISION. (b) MON of the product mixture as a function of the corresponding specific volume. The volume was increased by increasing the MCH conversion through RC and by combination of (RC + RO), see Table 4. Curves (a–c) represent the three Pt/HY + Ir/SiO₂ catalyst bed configurations illustrated in Fig. 8. Simulated RC composition at thermodynamic equilibrium as well as the specific volume of mixtures were calculated by using SimSci PRO/II PROVISION.

temperature reduction than the opening of the C₆-member rings. At the lowest temperatures investigated (533 K), case (c) presented the favorable situation of reaching a significant conversion of the RC products, while leaving the C₆-member ring almost unreacted. As the temperature increases, the direct opening of the C₆-member ring starts to occur on both reactor configurations, which generates the low-octane alkane products (*n*-heptane, 2-MH, 3-MH, and 3-EP). As a result, a desirable combination of the two reactors is one in which a high RC conversion is reached while avoiding the start of RO on the Pt/HY bed, followed by low temperature RO on the Ir/SiO₂ to effect the selective RO of the C₅-member rings, without opening the C₆-member rings.

If we evaluate the ratio of products with higher octane number than the feed to those with lower octane number than the feed, we see that this ratio decreases as the temperature increases. This trend is due to the higher activation energy on Ir/SiO₂ of those reactions that generate products of low ON. They are the direct opening of MCH and the cleavage of the RC products at the substituted C–C bonds (see Scheme 2). It has been demonstrated in previous studies that the breaking of substituted C–C bond has a higher activation energy than that of unsubstituted C–C bond via a dicarbene mechanism [37,19].

The effect of the different strategies on the resulting RON and MON can be compared in a more quantitative way by using the method developed by Ghosh et al. [32] and described above. As shown in Fig. 9(a and b) the RON and MON of the mixture for case (a) decreases as a function of conversion due to the direct opening of MCH, which as mentioned above generates alkanes of low RON and MON. By contrast, the RON and MON increases with conversion in cases (b and c) until it reaches a maximum and starts decreasing at high conversions (high temperatures), due to the contribution of direct MCH ring opening and cleavage of substituted C–C bonds, both producing low-RON/MON molecules.

Fig. 10(a and b) summarizes the resulting RON, MON, and specific volume of the product mixtures for the different

catalyst bed configurations. As mentioned, the most desirable outcome would be a product with RON/MON, as well as specific volume, higher than those of the feed. The results of the combined Pt/HY and Ir/SiO₂ with different extents of (RC + RO) reactions are compared to those of the Pt/HY and HY on which mostly RC occurs. Also, the values for an equilibrium mixture considering only RC products are included for comparison. The equilibrium has been calculated in the temperature range 373–773 K, which corresponds to a range of equilibrium conversions of 0–80. It can be observed that with RC alone, a significant increase in RON can be obtained reaching a maximum of 78. However, neither MON or specific volume are seen to increase much when no RO takes place. A significant gain in all three parameters can be obtained for the two configurations involving sequential beds at intermediate MCH conversion levels (i.e. 50–70%). Under these conditions, RON, MON, and specific volume are significantly higher than those of the feed. While RO does not impart a great enhancement in RON, it does benefit MON and specific volume.

4. Conclusions

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

- Ring opening of C₆-ring naphthenic molecules result in low-octane number products, while ring opening of C₅-rings can result in an increase, depending on which C–C bond is cleaved. Therefore, by combining the appropriate combination of ring contraction (RC) and ring opening (RO) catalysts one can maximize RON and MON.
- Pt/HY is an effective RC catalyst that can produce near-equilibrium RC products, without significant RO up to about 60% conversion. Increasing conversion on Pt/HY results in reduction in RON and MON, mostly due to RO of C₆-ring.
- Iridium is an active RO catalyst. By itself, it only results in RO of C₆-rings and therefore products of low RON and MON.

However, it may be effective in combination with Pt/HY which converts the C6-rings into C5-rings.

- The results obtained with combination of RC and RO catalysts (i.e. Pt/HY and Ir/SiO₂) showed that by using segregated catalyst beds with the RC catalyst preceding the RO catalyst it is possible to maximize the production of the iso-alkanes with the highest octane number (particularly MON).
- The combination of RC–RO is more effective than just RC only for the case of MON, while for RON there is no much advantage in adding the RO catalyst.

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