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Ring opening of 1,2- and 1,3-dimethylcyclohexane on iridium catalysts

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Abstract

The ring opening reactions of 1,2- and 1,3-dimethylcyclohexane (1,2- and 1,3-DMCH) have been investigated over Ir catalysts supported on Al_2O_3, SiO_2, and TiO_2. These two naphthenic molecules are used as probe reactants to investigate the different reaction paths that may occur in the treatment of diesel fuels and gasolines for the improvement of cetane numbers (CNs) and octane numbers. The CN can be improved by ring opening of naphthenics, but only when the C–C bond rupture occurs at a substituted position. Otherwise, the resulting product ends up with a high degree of branching, causing the CN to decrease. In this case, the octane number increases, which would be desirable in the production of gasolines. The present contribution shows that the preference of C–C bond opening at substituted or unsubstituted positions depends on the type of catalyst used, as well as on the nature of the reactant. Several ring-opening mechanisms can be operative under different conditions depending on the support used. For instance, the dicarbene reaction path results in C–C bond opening at unsubstituted positions and typically occurs on Ir/SiO_2 catalyst. In consequence, this catalyst may be desirable for increasing octane number while producing low-CN products. Two other mechanisms, those involving adsorbed olefin intermediates or metallocyclobutane intermediates, result in the C–C bond opening at substituted positions, which would be more desirable in the production of diesel fuel. Iridium on alumina has shown to be the most selective toward this type of ring opening. This preferred path on alumina-supported catalysts appears to be related to a support effect rather than to an effect of metal dispersion, because catalysts of different metal dispersions on alumina display a comparable selectivity much higher than that obtained on any of the silica-supported catalysts. To quantify these differences, a kinetic study was conducted by following the evolution of the *cis*- and *trans*-isomers of 1,2- and 1,3-DMCH as a function of space–time. The kinetic parameters obtained from this study indicate important disparities in the reactivity of the different isomers toward ring opening, and they depend strongly on the support used. To explain these disparities, it is proposed that dicarbene intermediates can be formed from all four isomers. However, only the two conformers that have diequatorial configurations (*trans*-1,3-DMCH and *cis*-1,2-DMCH) favor the formation of the intermediates leading to the SRO of substituted C–C bonds and hence to CN improvement.

Keywords: Cetane number; Octane number; Dimethylcyclohexane; Ring opening; Hydrogenolysis; Iridium catalysts; Ir/Al_2O_3; Ir/SiO_2.

1. Introduction

In response to the increasing demand for diesel fuel in the United States, the fraction of light cycle oil (LCO) added as a blending component to the diesel pool may increase greatly [1,2]. But LCO contains high concentrations of aromatics, which bear a very low cetane number (CN) and have a tendency to form soot in burning. Because the CN of LCO can be as low as 20, the imminent regulations for minimum CN in diesel fuels will represent a serious challenge to refiners currently investigating various hydrotreating strategies to upgrade LCO [3]. For example, a process consisting of two consecutive steps – initial hydrogenation of the aromatics to saturated cyclic compounds (naphthenics), followed by traditional hydrocracking of the saturated rings [4] – has been proposed to achieve this task. One problem associated with hydrocracking is that it produces a large fraction of low-molecular-weight products that cannot be used in diesel fuel.

A more novel approach has been recently proposed in which the deep hydrogenation step is followed by a process of selective ring opening (SRO) [5–9]. The main goal of the SRO reaction is to keep the same carbon number as the original naphthenic compounds while converting them to more paraf-

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finic compounds with expectedly higher CNs. However, as we have recently pointed out [10] not every ring-opening product (ROP) exhibits a CN higher than that of the naphthenic compound from which it originated. For example, the naphthenic decalin with two saturated C6 rings has a CN of about 36. If one of the two rings were opened selectively to yield butylcyclohexane, then the CN would increase to 47, but if the ring opening resulted in 1-isopropyl-2-methylcyclohexane, then the CN would decrease to about 24. In fact, in a typical acidic zeolite catalyst, the latter product is much more favorable than the former. A six-member ring is more difficult to open than a five-member ring. As a result, it is widely accepted that the ring opening of naphthenics on acidic catalysts proceeds via a ring-contraction step in which the six-member ring is converted into a five-member ring before opening [11,12]. The opening of the five-member ring can occur on acidic or metallic catalysts [13–15]. Over an acidic catalyst, the most favorable ring opening path occurs via beta scission at the C–C bond in the beta position from the tertiary carbon [15]. Consequently, the ROPs following this path result in branched molecules with low CNs, such as the 1-isopropyl-2-methylcyclohexane mentioned above. As first pointed out by Gault et al. more than 20 years ago [16,17], different ring opening mechanisms may operate over a metal catalyst. From studies conducted on Pt catalysts of varying particle sizes, these authors proposed that highly dispersed Pt catalysts favor C–C bond cleavage via a π-adsorbed olefin, whereas Pt catalysts of low dispersion follow the so-called "dicarbene reaction" path. The dicarbene reaction path results in cleavage of unsubstituted secondary–secondary C–C bonds. As in the case of acid-catalyzed C–C scission, this type of metal-catalyzed hydrogenolysis results in highly branched isoparaffins, which, as mentioned above, have low CNs and thus are undesirable for diesel fuel components. A third mechanism proposed by Gault et al. [17] involved a metallocyclobutane intermediate. Both the adsorbed olefin and metallocyclobutane reaction paths can result in C–C cleavage at substituted positions; therefore, either of these paths would be desirable for enhancing CN because the main consequence of cleaving a substituted C–C bond is the elimination of molecular branching. In contrast, if the fuel property that must be enhanced or preserved is the octane number, as for gasoline, then a catalyst that enhances the dicarbene path would be preferred, because this ring opening mode preserves the substituted C–C bonds and, consequently, molecular branching.

In recent publications and a series of patents, McVicker et al. [5–9], reported the high ring opening activity of Ir catalysts on six-member ring naphthenics. They pointed out the propensity of Ir to cleave C–C bonds via the dicarbene mechanism. In the present paper, we extend this study in the light of the approach described above; that is, we attempt to maximize the cleavage of substituted C–C bonds to enhance CN. We explore the effects of varying the support and the reduction temperature of iridium catalysts to investigate which of these effects has the greatest impact on the selectivity toward compounds with reduced branching (i.e., higher CN). We compare different Ir catalysts for the hydrogenolysis of 1,2- and 1,3-dimethylcyclohexane (DMCH). We also quantify the differences in reactivity and selectivity of the cis and trans isomers of these compounds in a kinetic study. Although these two reactants are outside the typical diesel range, we chose them as probe molecules for this study to better characterize the differences in selectivity and reactivity that may be encountered in an actual feed, while keeping the number of primary and secondary products sufficiently low to make a detailed analysis feasible.

2. Experimental

2.1. Catalyst preparation

A series of supported 0.9 wt% Ir catalysts were prepared by incipient wetness impregnation of different supports with aqueous solutions of $IrCl_3 \cdot 3H_2O$ (obtained from Alfa-Aesar) at appropriate Ir concentrations to yield 0.9 wt% loading while maintaining incipient wetness conditions for each support (with liquid/solid ratios for silica, alumina, and titania of 1.2, 0.9, and 0.5 mL/g, respectively). The support materials were silica (HiSil-210; PPG), γ-alumina (HP-140; Sasol), and titanium dioxide (P25; Degussa). After impregnation, the catalysts were dried overnight in the oven at 373 K and then calcined at 573 K for 2 h in air.

2.2. Catalyst characterization

The metal dispersion of the different catalysts was estimated from CO and H_2 chemisorption measurements. The former were conducted in a flow cell by the dynamic adsorption method, and the latter were done in a static apparatus by the standard volumetric method.

2.2.1. CO chemisorption

In each run, the catalysts were first reduced in H_2 at 723 K or 593 K for 1.5 h, then purged in He for 0.5 h at 723 K (or 593 K), and finally cooled under He to room temperature. Subsequently, consecutive CO pulses were sent over the sample while the intensity of the $m/e = 12$ mass signal at the outlet of the catalyst bed was monitored by mass spectrometry. When the area of the peak corresponding to each CO pulse did not vary within $\pm 1\%$, that value was taken as the total number of CO moles in the pulse, and consequently the CO/Ir ratio was obtained directly from the difference between the number of CO moles sent over the sample and those coming out, divided by the moles of Ir in the sample. Due to the formation of carbonate species that mask the true CO/Ir values, CO chemisorption values were not used for Ir/TiO_2 samples.

2.2.2. H_2 chemisorption

Reversible and irreversible hydrogen uptakes at 300 K were measured by the volumetric technique. Catalysts were treated in H_2 at 593 K or 723 K for 2 h and then evacuated at the same temperature for 0.5 h before the chemisorption measurements were obtained. After treatment, the samples were cooled to 300 K, and the first H_2 chemisorption isotherm was measured at 1–100 Torr H_2. A second isotherm was obtained after the

Table 1
Characteristics of the 0.9 wt% Ir catalysts investigated

Catalysts	Reduction temperature (K)	H/Ir	CO/Ir	Mesh size	BET area (m^2/g)
Ir/Al_2O_3-HD	723	1.20	0.73	150	250
Ir/Al_2O_3-LD	723	0.45	–	150	255
Ir/Al_2O_3-LD	723	0.45	–	20–40	255
Ir/SiO_2-HD	673	1.00	–	20–40	320
Ir/SiO_2-MD	593	0.27	0.27	150	120
Ir/SiO_2-LD	723	0.04	0.11	150	120
Ir/TiO_2-HD	593	1.50	–	150	50
Ir/TiO_2-LD	723	0.33	–	150	50

BET Surface area obtained by nitrogen adsorption/desorption. Chemisorption data obtained at room temperature after reduction at various temperatures. The suffix HD, MD, or LD is used to indicate high, medium, or low metal dispersion.

sample was evacuated at 300 K for 0.5 h. These two isotherms were extrapolated to zero H_2 pressure, and their difference was defined as the irreversible chemisorbed hydrogen and used to calculate the reported H/Ir values.

2.3. Catalytic activity measurement and data analysis

The ring opening reaction of 1,2- and 1,3-DMCH (obtained from Sigma-Aldrich) was carried out at 593 K under a total pressure of 3540 kPa, maintaining a molar ratio of hydrogen/hydrocarbon of 30. The runs were conducted in a plug-flow reactor consisting of a $\frac{1}{2}$-inch stainless steel tube placed inside an electric furnace equipped with a three-zone temperature controller. In all runs, the catalyst bed was kept isothermal. Hydrogen and liquid hydrocarbon were brought in contact in the co-current mode. The liquid was continuously fed into the reactor using an Isco LC-5000 high-pressure syringe pump operating in the volumetric flow rate range of 0.15–400 mL/h. Before each run, the catalyst was reduced in hydrogen flow at 723 K (or 593 K in the case of low-temperature reduction) for 2 h and then cooled to the reaction temperature (593 K). Recently, a study on the ring opening of naphthenics on Ir catalysts conducted at atmospheric pressure reported that the products were dominated by dehydrogenated compounds (xylenes), coke, and deep hydrogenolysis products (e.g., C1, C2) [18]. Those products were not observed in the current study, which was conducted at high pressure, at a high hydrogen/hydrocarbon ratio, and with negligible catalyst deactivation.

The products were collected as liquid in a dry ice in acetone bath, with the temperature kept at 197 K to capture all of the products. The liquid product was manually injected into a Hewlett-Packard 5890 Plus GC for composition analysis. A Shimadzu GC-MS-QP5000 was used to identify the products with maximum certainty. Analysis of the numerous products obtained in this conversion is not straightforward, and many standard compounds were used to confirm the identity of the compounds.

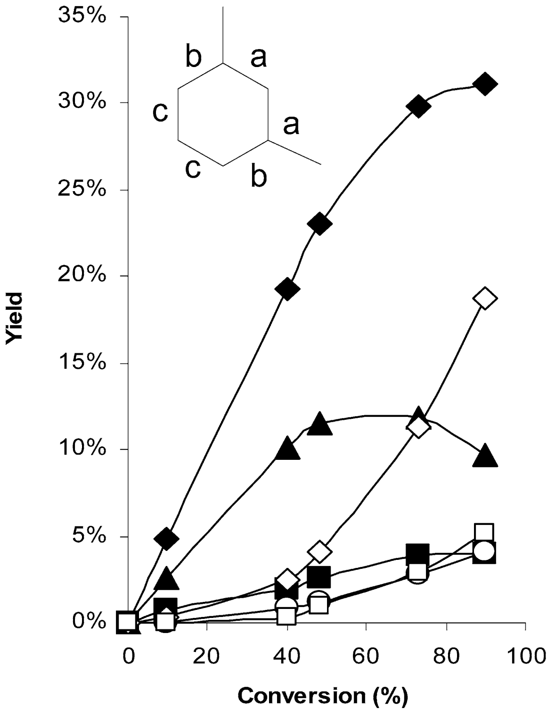


Fig. 1. Yield of RO products from 1,3-DMCH on Ir/Al_2O_3-HD catalyst. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Error bar 2–3%. Primary products: ▲, 2-MC7 (from *a*); ■, 4-MC7 (from *b*); ◆, 2,4-DMC6 (from *c*). Secondary products: ○, 2-MC6 (2-MC7); □, 3-MC6 (4-MC7); ◇, 2,4-DMC5 (2,4-DMC6).

3. Results

3.1. Chemisorption of hydrogen and carbon monoxide

Table 1 summarizes the characteristics of the catalysts investigated, including BET surface areas, chemisorption uptakes, and particle mesh size for the pellets (20–40 mesh) or powders (150 mesh) used. Several catalysts of varying metal dispersion were prepared by varying the surface area of the support or the reduction temperature. As expected, the Ir/SiO_2 and Ir/TiO_2 catalysts reduced at low temperature had higher hydrogen and CO uptakes than those reduced at high temperature, as a result of particle sintering and, in the case of TiO_2, the partial encapsulation occurring at 723 K [19]. As can be observed, some of the most highly dispersed catalysts display H/Ir values > 1, as typically observed by other researchers working with supported Ir catalysts [20].

3.2. Ring opening of 1,3-DMCH

As illustrated in Fig. 1, the ring opening of 1,3-DMCH over the highly dispersed Ir/Al_2O_3 catalyst generates three primary products: 2-methylheptane (2-MC7), 4-methylheptane (4-MC7), and 2,4-dimethylhexane (2,4-DMC6), which are designated in Fig. 1 as products resulting from C–C opening of positions *a*, *b*, and *c*, respectively. Whereas 2-MC7 and 4-MC7 arise from the breakage of tertiary-secondary C–C bonds (*a* and *b*), 2,4-DMC6 is formed by cleavage of a secondary–secondary C–C bond (*c* in the Fig. 1). As described in a recent contribution [10], using an artificial neural network and a database of all of the available experimental CN data [21], we were able to predict the CNs of products, such as those indicated by *a*, *b*, and *c* (47, 40, and 31, respectively). These estimations are in good agreement with observations by Wilson et al. [22], who indicated that molecules with high CH_3/CH_2 ratio (i.e., highly branched compounds) have low CN. Starting with a CN of the original feed of 30, cleavage at both the *a* and *b* positions, but not at *c*, results in desirable products.

Fig. 1 shows the yields of the different products as functions of conversion. The evolution of yield vs. conversion clearly shows that, as expected, 2-MC7 (from cleavage in *a*), 4-MC7 (from cleavage in *b*), and 2,4-DMC6 (from cleavage in *c*) are the only primary products, as evidenced by the nonzero derivative at low conversions. In contrast, 2-MC6 and 2,4-DMC5 are secondary products resulting from sequential hydrogenolysis of the primary products. From these data, we were able to obtain the ratio of desirable $(a + b)$ to undesirable *c* cleavage for the different catalysts. This ratio $(a + b)/c$ could be obtained from the ratio of (2-MC7 + 4-MC7)/2,4-DMC6 if there was no secondary hydrogenolysis. However, the (2-MC7 + 4-MC7)/2,4-DMC6 ratio decreases as a function of conversion. The pronounced decrease of this ratio with conversion can be due to a faster conversion of the longer-chain methylheptanes (2-MC7 and 4-MC7) than the more branched dimethylhexane (2,4-DMC6). Then the value of the ratio at low conversions (i.e., when secondary reactions are negligible) can be taken as a measure of the intrinsic ability of a catalyst to cleave substituted C–C bonds.

Looking for a catalyst with high-cetane selectivity [i.e., the highest $(a + b)$ compared with *c*], we tested three different supported catalysts, all of which were reduced at 723 K. As shown in Fig. 2, there is a dramatic difference in the substituted/unsubstituted bond cleavage ratio when the support is varied. The observed trend is as follows: $Ir/Al_2O_3 \approx Ir/TiO_2 \gg Ir/SiO_2$. Thus, for CN improvement, titania or alumina supports should be used. Conversely, if the desired property is the octane number, then the most effective support would be silica.

Furthermore, we have observed that the chance of breaking the substituted C–C bond inside (position *a*) and outside (position *b*) the two methyl groups also varies when the support is changed. The ratio a/b is also important, because there is a significant difference in the CN of the product obtained by each of the two substituted C–C bonds. Opening at position *a* gives 2-MC7 (CN = 47), whereas opening at position *b* gives 4-MC7 (CN = 40); thus a high a/b ratio is desirable. As shown in Fig. 3, the Ir/Al_2O_3 catalyst shows the highest (2-MC7/4-MC7) ratio (i.e., corresponding to a/b at low conversions), but this ratio decreases significantly with increasing conversion due to the secondary hydrogenolysis of the primary products. Meanwhile, this ratio stays relatively constant for the other two catalysts. If there were no preferential cleavage for the two possible substituted C–C bonds, then the statistical ratio for a/b would be equal to unity $(2/2)$. However, as shown in this figure, the ratio is >2 at all conversions and can be as high as 4 for some catalysts at low conversions. It is then concluded that the C–C bond inside the two methyl substituents (*a*) is preferentially ruptured in comparison with the C–C bonds outside the groups (*b*).

It is well known that increasing the reduction temperature of a supported metal catalyst typically results in increased particle size. It is also known that significant losses in hydrogen uptake are observed on noble metal catalysts supported on TiO_2; however, these are due not to growth of the metal clusters, but rather to partial encapsulation by the support [23]. Therefore, we have investigated the effect varying the reduction temperature on the product distribution of Ir/SiO_2 and Ir/TiO_2 catalysts.

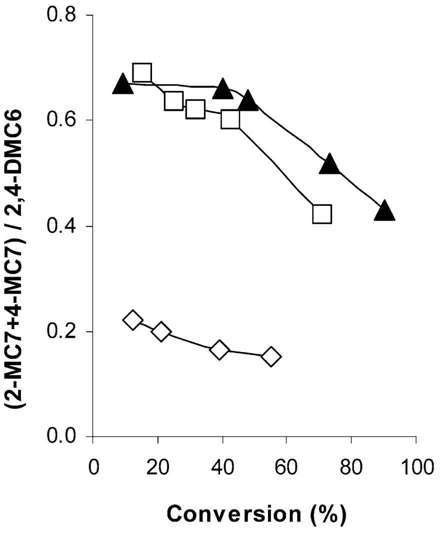


Fig. 2. Ratio of substituted C–C cleavage to unsubstituted C–C cleavage of 1,3-DMCH over Ir on different supports. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Without considering secondary hydrogenolysis, the ratio (2-MC7 + 4-MC7)/2,4-DMC6 would represent the ratio of $(a + b)/c$ cleavage; *a*, *b*, and *c* as defined in Fig. 1. The statistical value of $(a + b)/c$ is 2. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD; □, Ir/TiO_2-LD. Error bar 0.05.

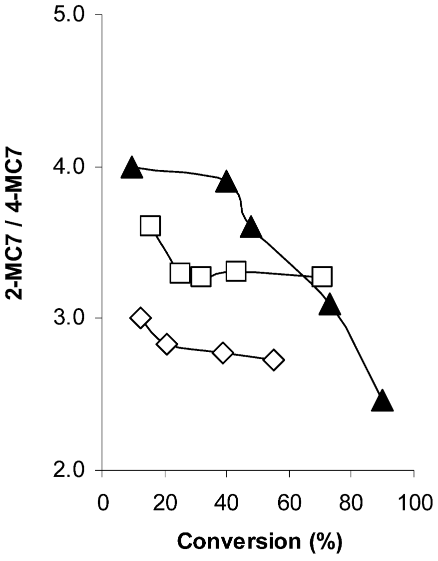


Fig. 3. Ratio of substituted C–C cleavage at internal to external positions of 1,3-DMCH over Ir on different supports. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Without considering secondary hydrogenolysis, the ratio 2-MC7/4-MC7 would represent the ratio of a/b cleavage; *a* and *b* as defined in Fig. 1. The statistical value of a/b is 1/1. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD; □, Ir/TiO_2-LD. Error bar 0.1.

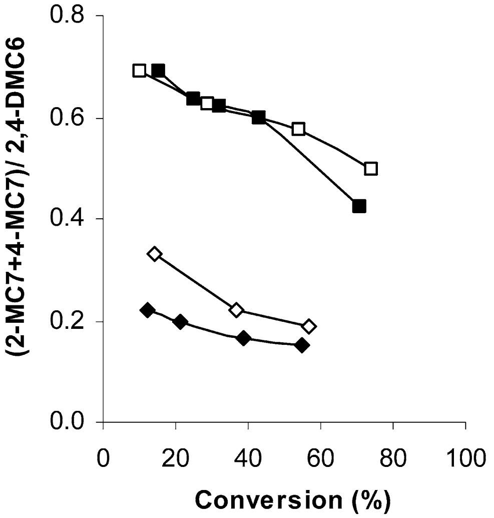


Fig. 4. RO of 1,3-DMCH: (2-MC7 + 4-MC7)/2,4-DMC6 ratio with LTR (593 K) and HTR (723 K) catalysts. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. ◇, Ir/SiO$_2$-MD; □, Ir/TiO$_2$-HD; ◆, Ir/SiO$_2$-LD; ■, Ir/TiO$_2$-LD. Error bar 0.02.

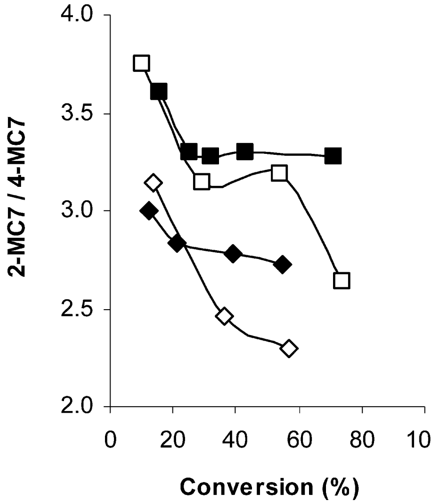


Fig. 5. Ratio of substituted C–C cleavage at internal to external positions of 1,3-DMCH over Ir catalysts reduced at different temperatures; LTR = 593 K; HTR = 723 K. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Without considering secondary hydrogenolysis, the ratio 2-MC7/4-MC7 would represent the ratio of a/b cleavage; a and b as defined in Fig. 1. The statistical value of a/b is 1/1. ◇, Ir/SiO$_2$-MD; □, Ir/TiO$_2$-HD; ◆, Ir/SiO$_2$-LD; ■, Ir/TiO$_2$-LD. Error bar 0.05.

As described above, the $(a + b)/c$ ratio represents the ability of the catalysts to cleave substituted C–C bonds. Fig. 4 shows the evolution of the (2-MC7 + 4-MC7)/2,4-DMC6 ratio as a function of conversion for the two catalysts after low- and high-temperature reduction. Whereas for the case of TiO$_2$-supported catalysts there was little difference between low-temperature and high-temperature reduction, a substantial loss in selectivity was observed on the SiO$_2$-supported catalyst after reduction at 723 K. It is possible that the high-temperature reduction causes a greater decrease in metal dispersion on the SiO$_2$-supported catalyst.

Similarly, the 2-MC7/4-MC7 ratios shown in Fig. 5 for these two catalysts after different reduction treatments seem to differ significantly as a function of reduction temperature. Although the effect of reduction temperature is not significant at low conversions, the difference becomes more pronounced with increasing conversion, indicating that the high-temperature reduction preferentially inhibits the secondary hydrogenolysis of 2-MC7. As a result, the 2-MC7/4-MC7 ratio does not decrease as much with conversion over the catalysts reduced at high temperature as over the catalysts reduced at lower temperatures, which is advantageous in maintaining a higher CN. As mentioned above, this variation is not so much due to a change in the intrinsic rate of ring opening by the two different modes, but rather to a change in secondary conversion of the ROPs.

3.3. *Ring opening of 1,2-DMCH*

The ring opening of 1,2-DMCH is another interesting reaction that may result in products with dramatic differences in CN, depending on the specific bonds cleaved. For example, as illustrated in Fig. 6, n-octane (n-C8) and 3-methylheptane (3-MC7) are obtained by cleavage of substituted C–C bonds at positions a and b, respectively. In contrast, cleavage of unsubstituted C–C bonds (positions c and d) produces 2,3- and 3,4-DMCH, respectively. The difference in the CNs of these products is dramatic; that is, starting with a feed of 1,2-DMCH, with CN = 22, the products obtained by cleavage at a, b, c, and d positions have CNs of 64, 43, 29, and 27, respectively. It is easily seen that a huge gain in CN can be achieved if substituted C–C bonds are preferentially cleaved.

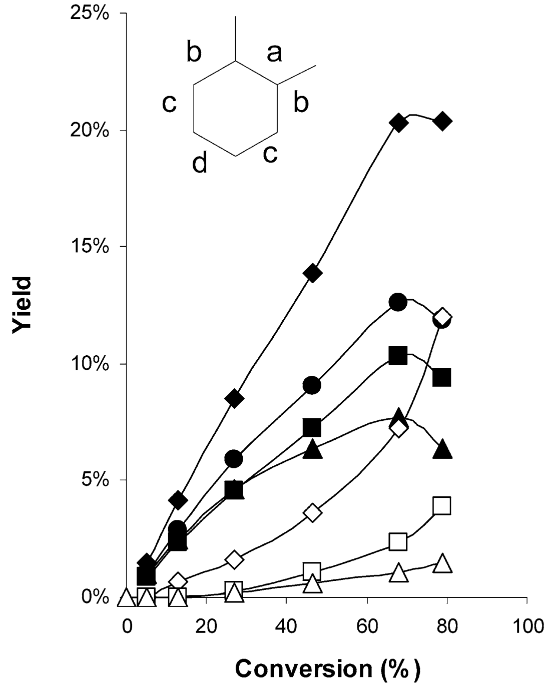


Fig. 6. RO of 1,2-DMCH on Ir/Al$_2$O$_3$-HD catalyst. Product yields at different conversion. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Error bar 1% Primary products: ▲, n-C8 (from a); ■, 3-MC7 (from b); ◆, 2,3-DMC6 (from c); ●, 3,4-DMC6 (from d). Secondary products: ◇, 2,3-DMC5 (from 2,3-DMC6); ○, 3-MC6 (from 3MC7); n-C7 (from n-C8).

From the evolution of products shown in Fig. 6 as a function of conversion for the case of the Ir/Al_2O_3 catalyst, it can be concluded that, as in the case of 1,3-DMCH, the primary products are those on which only one C–C cleavage occurs, that is, *n*-C8, 3-MC7, and 2,3- and 3,4-DMCH. In contrast, those with lower numbers of carbons, 3-methylhexane (3-MC6) or 2,3-dimethylpentane (2,3-DMC5), are clearly secondary products (i.e., zero derivative at $x = 0$). Accordingly, the $(a + b)/(c + d)$ ratio indicates the relative rate of substituted to unsubstituted C–C cleavage. The (n-C8 + 3-MC7)/(2,3-DMCH + 3,4-DMCH) ratio is shown in Fig. 7 as a function of conversion for two different catalysts. Following a similar trend, but even more clear than that shown in the previous case, the Ir/Al_2O_3 catalyst stands out as the most selective catalyst toward the desired products. In contrast, the SiO_2-supported catalyst shows again a strong preference for breaking the unsubstituted C–C bonds and consequently producing less desirable products.

Like other *n*-alkanes, *n*-C8 has a very high CN; therefore, finding a catalyst that is particularly selective for producing *n*-C8 would be highly desirable. However, as shown in Fig. 8, in the case of 1,2-DMCH, the *n*-C8/3-MC7 ratio, corresponding to a/b at low conversions, is rather insensitive to the catalyst used and only varies with conversion. This behavior is in contrast to the opening of 1,3-DMCH, in which the ratio of internal to external substituted C–C bond cleavage (i.e., a/b ratio) was a strong function of the catalyst used. That is, from the previous results, the Al_2O_3-supported catalyst would be expected to yield a higher ratio of a/b compared with the SiO_2-supported catalyst. But in fact this is not the case; the *n*-C8/3-MC7 ratio starts above 1 and approaches 0.5 as the conversion increases for all of the catalysts. The statistical value for the a/b ratio is 0.5, indicating that the cleavage of the C–C bond between the two methyl groups is preferred compared with the cleavage of the C–C bonds external to the methyl groups. On the other hand, for the unsubstituted C–C cleavage products, the ratio of c/d varies with the catalyst used and in all cases is lower than the statistical value of 2.0 (see Fig. 9 at low conversion). Another difference between Ir/SiO_2 and Ir/Al_2O_3 catalysts is that on the former, the 2,3-DMCH/3,4-DMCH ratio does not vary with conversion, but on the latter the ratio is greatly increased. This difference indicates that whereas on alumina-supported Ir, the consumption of 3,4-DMCH by secondary hydrogenolysis is higher than that of 2,3-DMCH, on the silica-supported catalyst, both primary products are consumed equally.

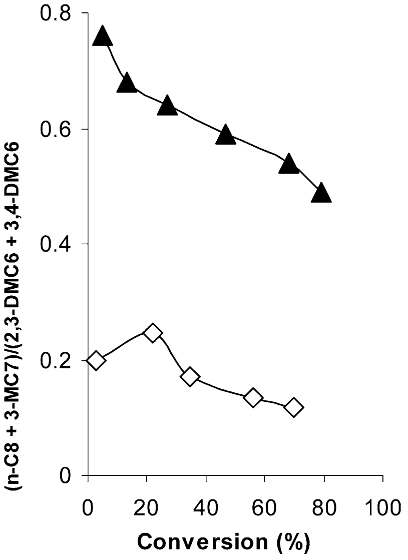


Fig. 7. RO of 1,2-DMCH: (n-C8 + 3-MC7)/(2,3-DMC6 + 3,4-DMC6) ratio with different supported catalysts. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD. Error bar 0.05.

The ultimate goal of ring opening is to improve the CN. Here we have concentrated on dimethylcyclohexane as a probe molecule, but the results should be also valid for larger molecules,

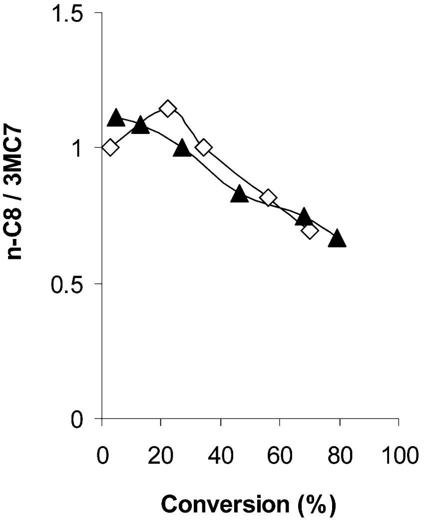


Fig. 8. RO of 1,2-DMCH: n-C8/3-MC7 ratio. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. Error bar 0.1. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD; statistical value n-C8/3-MC7 = 0.5.

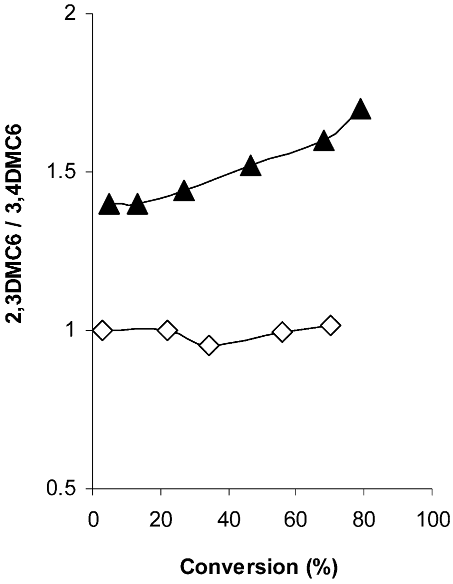


Fig. 9. RO of 1,2-DMCH: 2,3-DMC6/3,4-DMC6 ratio. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD; statistical value 2,3-DMC6/3,4-DMC6 = 2. Error bar 0.1.

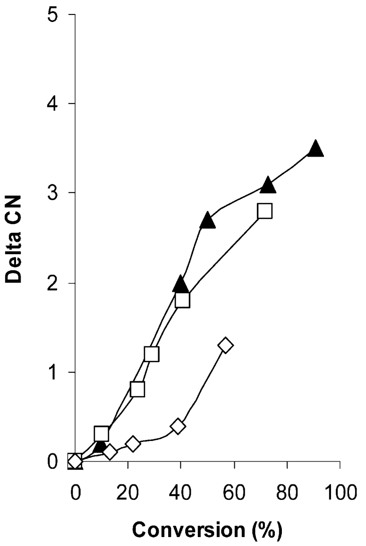


Fig. 10. RO of 1,3-DMCH: Delta CN vs. conversion. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD; □, Ir/TiO_2-LD. Delta CN = difference in the overall CN and the original CN of the feed.

more typical of diesel fuels. That is, as reported previously [10], the presence of alkyl branching in the final product greatly reduces the resulting CN; similarly, the shortening of alkyl chains also lowers the CN. Therefore, it is important to evaluate how the CN varies as a function of conversion over different catalysts. Having the tool that allows us to predict the CN for all the products that are obtained in the ring opening, we can calculate the overall CN for different catalysts at various conversions by making the simplifying assumption that the overall CN is a linear combination of the individual CNs in the mixture. Figs. 10 and 11 show the change in CN during the ring opening of 1,2- and 1,3-DMCH, respectively. The overall CN increases with conversions for all tested catalysts. The maximum CN improvement is observed for the alumina-supported catalyst, that is, 3.5 for 1,3-DMCH and 9.0 for 1,2-DMCH. The cetane value of the latter is more positively impacted due to the larger difference in CN between the products and the feed. The maximum difference between a product (n-C8) and the feed for 1,2-DMCH is 42 cetane points; in contrast, the maximum difference for 1,3-DMCH is only 17 points. Because the alumina-supported catalyst causes the highest ratio of substituted/unsubstituted C–C bond cleavage, it results in the greatest CN enhancement. The CN does not improve as much on the silica-supported catalyst, because of the large amount of highly branched products originating from unsubstituted C–C bond cleavage, which is the preferred RO mode on this catalyst. As mentioned above, even on the most selective catalyst, the observed increase in CN is rather modest due to the secondary hydrogenolysis that occurs preferentially on the most desirable (for diesel fuels) long-chain products. A remaining challenge is to find a catalyst that can selectively open the substituted C–C bonds without further breaking the paraffinic products.

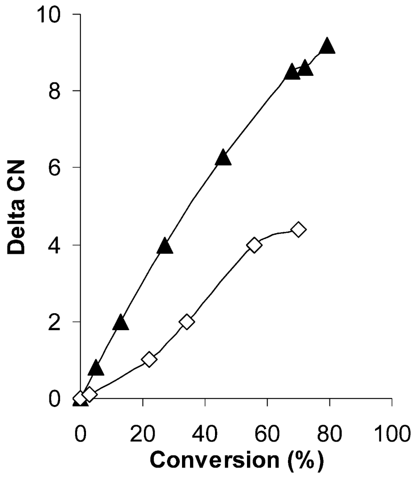
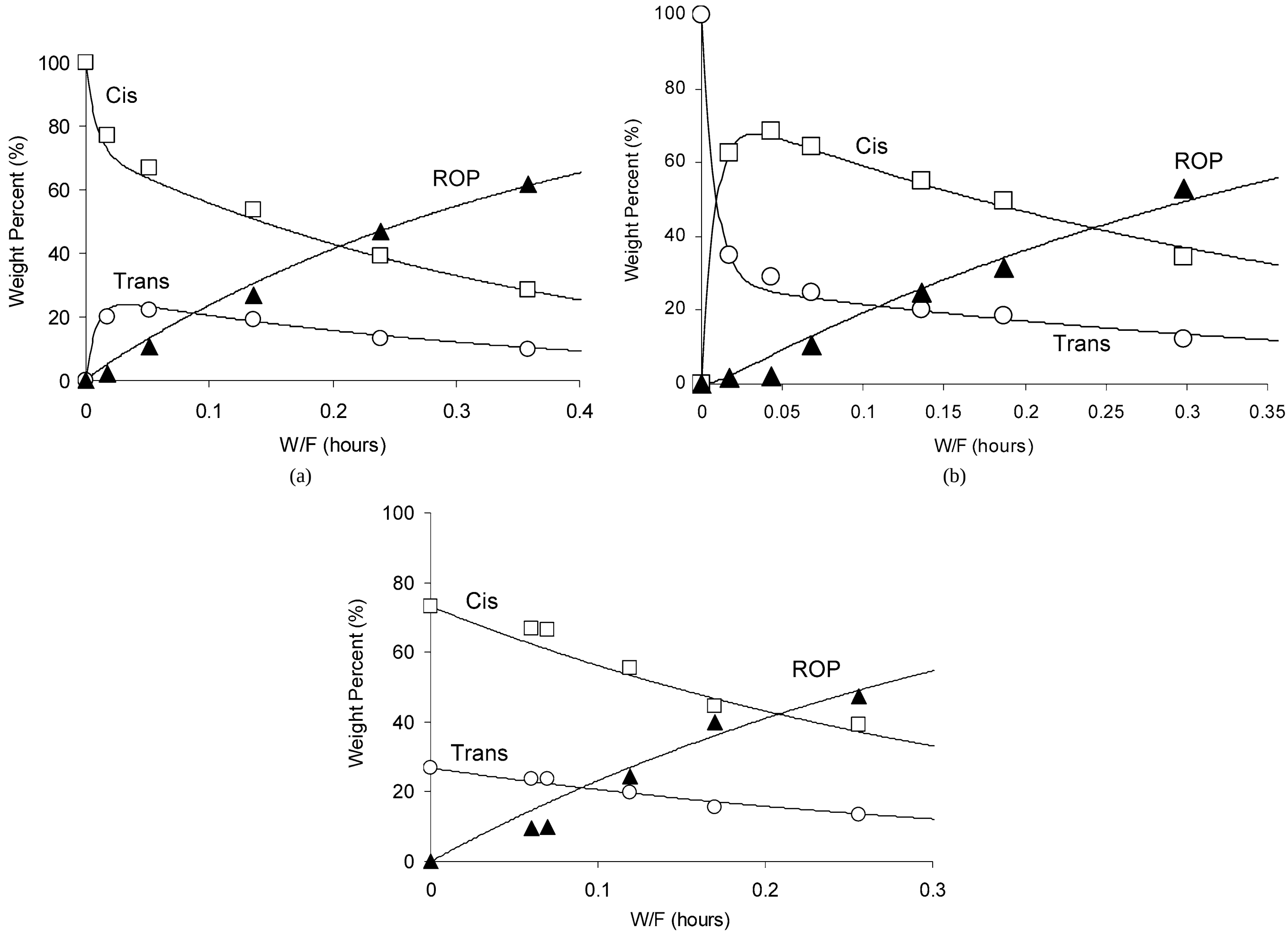


Fig. 11. RO of 1,2-DMCH: Delta CN vs. conversion. Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. ▲, Ir/Al_2O_3-HD; ◇, Ir/SiO_2-LD. Delta CN = difference in the overall CN and the original CN of the feed.

3.4. Conversion of 1,2-DMCH and 1,3-DMCH as a function of W/F

The evolution of conversion with space–time (W/F) was investigated for the two reactants, 1,2-DMCH and 1,3-DMCH, paying particular attention to the potentially different reactivity of the cis and trans isomers of the two reactants. The reactions were carried out at varying space-time (W/F), isothermally at 593 K, under a total pressure of 3540 kPa and keeping a hydrogen/hydrocarbon ratio of 30. Four different feeds were investigated: pure *cis*-1,3-DMCH, pure *trans*-1,3-DMCH, a 73/27 mixture of *cis*/*trans* 1,3-DMCH, and a 86/14 mixture of *cis*/*trans* 1,2-DMCH. To compare the reactivity of the cis and trans isomers, we followed the evolution of each of the two isomers, while lumping all the RO products into one. The evolution of concentrations as a function of W/F is shown in Figs. 12a, b, and c for 1,3-DMCH and in Figs. 13a and b for 1,2-DMCH. To get a quantitative measure of the different reactivities, four reactions were taken into consideration for each reactant: *cis*-to-*trans*, *trans*-to-*cis*, *cis*-to-ring opening, and *trans*-to-ring opening (see Table 3). Assuming a first-order dependence on the reactant concentration for each of these reactions, very good fitting of the evolution of concentration with space–time was obtained using the rate constants as fitting parameters. It must be emphasized that for 1,3-DMCH, the fit was done simultaneously for the different feeds (e.g., pure *cis*, pure *trans*, and the mixture); that is, only one set of apparent reaction constants was obtained, but these represent the fitting of three sets of data. As summarized in Table 3, the stability and reactivities of the cis and trans isomers follow opposite trends for 1,3-DMCH and 1,2-DMCH. That is, *cis* is the thermodynamically more stable isomer for 1,3-DMCH, and *trans* is the thermodynamically more stable isomer for 1,2-DMCH. At the same time, whereas the conversion to ROP is favored with *cis*-1,3-DMCH, the opposite is true with 1,2-DMCH; that is,



(a)

(b)

(c)

Fig. 12. RO of *cis*- (a), *trans*- (b), and mixture (c) 1,3-DMCH on Ir/Al_2O_3-HD catalyst. Product compositions at different W/F (symbol, experimental; line, fitting). Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30.

trans-1,2-DMCH is more reactive toward ROP than *cis*-1,2-DMCH.

A dramatic effect of the support is demonstrated for the ring opening of 1,2-DMCH. Whereas on the SiO_2-supported Ir catalyst, the ring opening rate is less than twice as high as for *trans* as for the *cis* isomer, on the Ir/Al_2O_3, this ratio is >15. This dramatic difference is discussed in the next section.

4. Discussion

4.1. Ring opening mechanisms on different catalysts

Ring opening appears to be an attractive process for increasing CN and at the same time increasing diesel volume, without significant losses in molecular weight. However, not every ROP exhibits a high CN. Therefore, controlling the specific type of C–C bond cleaved is very important. For instance, over metal catalysts, different ring opening mechanisms may result in products of higher or lower CN than the original naphthenic molecule. The dicarbene mechanism results in C–C cleavage of unsubstituted secondary–secondary carbon atoms, producing highly branched isoparaffins with low CN. In contrast, both the π-adsorbed olefin and metallocyclobutane reaction mechanisms can achieve C–C cleavage at substituted positions, which eliminates branching and enhances the CN. As reported by Gault et al. [17] hydrogenolysis of the endocyclic C–C bond on Pt catalysts can proceed through either dicarbene or π-adsorbed olefin. These authors showed that the predominance of each mechanism depends strongly on the Pt particle size. The π-adsorbed olefin mode requires flat adsorption of three neighboring carbon atoms, whereas the dicarbene mode requires metal–carbon bonding of two carbon atoms, with the molecule adsorbed perpendicular to the surface (see the scheme). Moreover, these authors proposed that the latter mechanism is favored when big ensembles of active sites are available, whereas as the particle size grows or big clusters of atoms are broken up by surface dilution, the dicarbene mode is suppressed, and consequently the π-adsorbed olefin mechanism becomes dominant.

On Rh catalysts, the effect of particle size on the operating ring opening mechanism has been well studied for the case of methylcyclopentane (MCP) hydrogenolysis [24–27]. In this case, the dicarbene mechanism was clearly evident when large ensembles were present, with 2-methylpentane and 3-

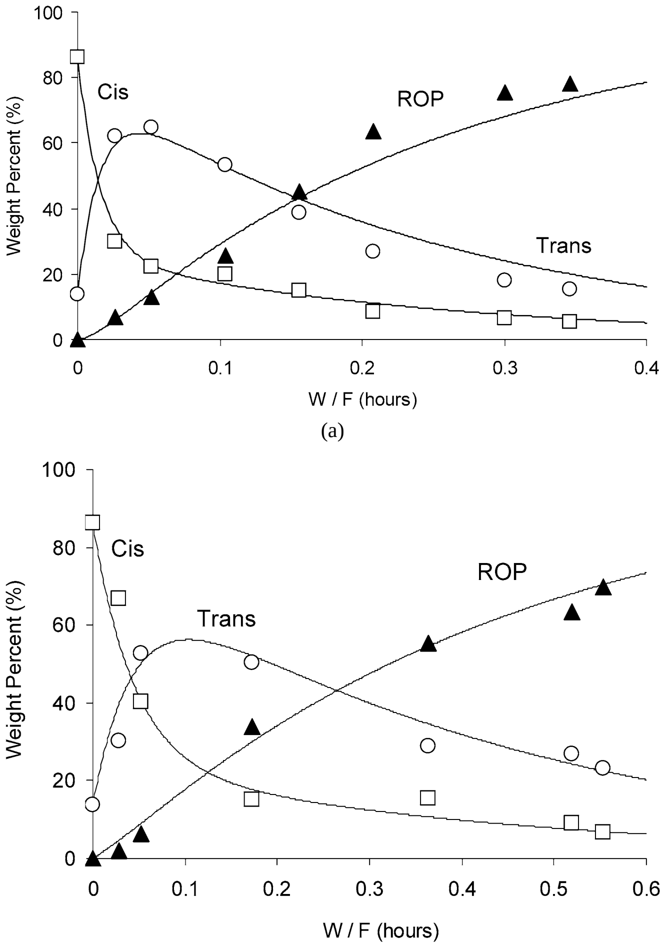
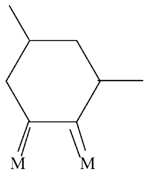


Fig. 13. RO of 1,2-DMCH on Ir/Al_2O_3-HD (a) and Ir/SiO_2-LD (b) catalysts. Product compositions at different W/F (symbol, experimental; line, fitting). Reaction was conducted at 593 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30.

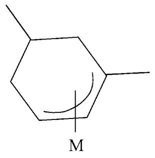
methylpentane the dominant products. In contrast, on small particles, the statistical distribution was typically observed, and the product of substituted C–C cleavage (n-hexane) was obtained in significant quantities. Similarly, the use of bimetallic catalysts demonstrated a similar shift to more substituted C–C cleavage as the density of the large ensemble of sites was diluted with unreactive metals [28,29].

Within a series of noble metals investigated by Gault et al. [30], iridium displayed the strongest tendency to break unsubstituted C–C bonds; that is, Ir exhibited a strong preference for the dicarbene mechanism. Moreover, this tendency did not change with particle size, in direct contrast with the behavior of Pt, which typically shows a dramatic effect of metal dispersion. Likewise, Ponec et al. [31] found no significant effect of particle size in ring opening reactions over Ir catalysts of various dispersions, but reported that Ir became more selective toward ring opening at substituted (tertiary) carbon centers as the catalyst became covered by carbonaceous species. They proposed that the presence of carbon on the surface eliminated the large ensembles of contiguous atoms and suppressed the formation of dicarbene intermediates. Therefore, it is possible that carbon deposition can mask the true structure sensitivity of these reactions. In the present study, we found strong support and particle size effects in the selectivity to substituted C–C bond rupture compared with unsubstituted C–C bonds under high hydrogen pressure conditions, which are conducive to a low rate of coke formation and negligible catalyst deactivation.

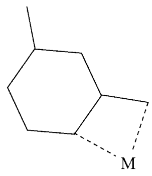
Whenever the catalyst structure is such that allows any of the two reaction paths to operate, the reaction will proceed through the path with the lowest activation energy. According to Foger et al. [32,33] the activation energy for the dicarbene mode is significantly lower than that for the π-adsorbed olefin mode. These authors observed an activation energy of 170 kJ/mol for the n-butane hydrogenolysis, a typical dicarbene reaction, and a much higher activation energy (240 kJ/mol) for the hydrogenolysis of neopentane, in which the dicarbene mode is not possible. In addition to these two typical mechanisms for ring opening of C5 and C6 rings, Gault et al. [34] proposed an alternative one that would operate via a metallocyclobutane intermediate consisting of a metal atom and four C atoms that would allow the opening of substituted C–C bonds if an external methyl group were involved in the intermediate. The schemes shown below represent the three different modes of ring opening (dicarbene, π-adsorbed olefin, and metallocyclobutane)



(**I**) Dicarbene mode



(**II**) π-Adsorbed olefin mode



(**III**) Metallocyclobutane mode

According to Gault et al. [34], the reaction path involving the metallocyclobutane intermediate would have an activation energy higher than that involving the dicarbene intermediate. Therefore, this path could operate only when the lower-energy dicarbene path was blocked. Recently Coq et al. [35] proposed that the metallocyclobutane mechanism is operative in the hydrogenolysis of 2,2,3,3-tetramethylbutane on Ru catalysts, because the structure of this molecule is particularly well suited for the formation of metallocyclos rather than dicarbenes.

Iridium is known to exhibit low isomerization activity on nonacidic supports [36,37]. Yet, it may be conceivable that, in addition to the direct hydrogenolysis paths described above, an intermediate C6 ring-to-C5 ring isomerization step can occur to convert dimethylcyclohexanes into alkylcyclopentanes, which would subsequently undergo C5 ring opening. However, several experimental observations in this work indicate that this path may not make a significant contribution. In the first place, no C5 ring product was observed at any conversion level. Moreover, had a C5 ring intermediate been formed and then cracked, then we should have observed isoparaffins such as 3,4-dimethylhexane or 3-ethyl-2-methylpentane. These two isoparaffins would have been expected had 1,3-DMCH isomerized to the most favorable 1-ethyl-2-methylcyclopentane and then ring opened at the most favorable dicarbene positions. Neither these or any of the other possible secondary products that can arise only from ring opening of C5 rings were observed.

Table 2
Study of different support, metal dispersion and pellet size on selectivity toward substituted C–C bond cleavages in ring opening of 1,3-DMCH

Catalysts	H/Ir	Mesh size	BET area (m^2/g)	Conversion (%)	(2-MC7 + 4-MC7)/ 2,4-DMC6
Ir/Al_2O_3-HD	1.20	150	250	2.90	1.00
Ir/Al_2O_3-LD	0.45	150	250	1.00	0.90
Ir/Al_2O_3-LD	0.45	20–40	250	0.90	0.95
Ir/SiO_2-HD	1.00	20–40	320	1.00	0.45
Ir/SiO_2-LD	0.04	150	120	4.00	0.32

Reaction was conducted at 603 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30.

Finally, no significant differences in selectivity (see Table 2) were observed when the catalyst pellet size was varied from 20–40 mesh to a powder. Some changes in selectivity with pellet size might be expected had the reaction occurred in a series of steps involving stable intermediates such as C5 ring compound, which could desorb, diffuse through the pores, readsorb, and react on a different size. All of these observations point to toward one-step ring opening as the major primary reaction, in which the selectivity is determined by the specific C–C bond cleavage (i.e., either substituted or unsubstituted).

4.2. *Effect of methyl substituents*

Working on a series of highly-substituted cyclopentane molecules, Gault et al. [34] observed that the addition of methyl groups decreased the difference in activation energy between the metallocyclobutane and dicarbene modes. It is conceivable that this trend works not only for substituted cyclopentanes (C5 rings), but also for cyclohexanes (C6 rings), as used in the present work. In fact, McVicker et al. [5] did not observe a substantial opening of substituted C–C bonds in the hydrogenolysis of methylcyclohexane on Ir/Al_2O_3 catalysts, but did observe a significant degree of substituted C–C bond cleavage when the feed was 1,2,4-trimethylcyclohexane. This enhancement indicates that the metallocyclobutane mechanism may be operative, because this intermediate is the only one directly involving participation of the external methyl group (see the earlier scheme). Note that the enhancement is observed only on selectivity toward substituted C–C bond cleavage, and not on overall reactivity. In fact, we measured very similar total conversions comparing the reactivities of methylcyclohexane and dimethylcyclohexane at 553 K on the same Ir/Al_2O_3-HD catalyst.

In the present work we observe that the addition of methyl substituents not only enhances the rate of ring opening of C6 rings, but also contributes positively to the ring opening at sterically hindered C–C bonds. We find that C–C bonds internal to the two methyl groups (position a) are preferentially opened in comparison with the C–C bonds external to the substituents (position b). Figs. 3, 5, and 8 show that the observed ratios (a/b) are greater than the statistical values. This observation is in accordance with the results obtained by Gault et al. [17,34] in hydrogenolysis of 1,2- and 1,3-DMCP on 10 wt% Pt/Al_2O_3. They pointed out that the ratio of n-heptane/3-methylhexane and 2-methylheptane/3-methylheptane always stayed above the statistical 0.5 and 1.0, respectively.

Moreover, we observe that the addition of methyl substituents to the C6 ring not only affects a/b ratio but also the c/d ratio of the unsubstituted C–C bonds. As shown in Fig. 9, the c/d ratio is less than the statistical value of 2.0 on all of the catalysts investigated, indicating that the C–C bonds farthest away from the substituent methyl groups are more favored for cleavage. A similar result was obtained in the hydrogenolysis of MCP on Rh/TiO_2 and Rh/SiO_2 catalysts [24] and on Pt(111) [38], for which the observed 2-methylpentane/3-methylpentane ratio was much lower than the statistical value of 2.

4.3. *Reactivity of the cis- and trans-isomers of dimethylcyclohexane*

It is well known that the stability of the isomers of 1,3- and *trans*-1,2-DMCH follow opposite trends. In 1,2-DMCH, the *cis*-isomer always has one methyl in the axial position and one methyl in the equatorial position. Therefore *cis*-1,2-DMCH is less stable than *trans*-1,2-DMCH, which can be diequatorial, and so it minimizes the substituent–substituent interactions. The opposite is true in 1,3-DMCH, in which the methyl groups of the *cis*-isomer can be either both equatorial or both axial. The latter conformation is much less stable, however; almost all of the *cis*-isomer is diequatorial, and thus *cis*-1,3-DMCH is more stable than *trans*-1,3-DMCH. The relative stability of the different isomers correlates well with the values of rate constants that we obtained for the *cis*-to-*trans* reactions with the two different reactants.

Similar trends in isomerization rates were observed by Bratok et al. [39] working with a series of dimethylcyclohexane isomers on a Pt/SiO_2 catalyst. What has not been reported before is the quantification of the relative rates of ring opening of the various isomers. For example, we observed that *cis*-1,3-DMCH is more reactive toward ring opening than the *trans*-isomer, but *trans*-1,2-DMCH is more reactive toward ring opening than the *cis*-isomer. To explore these differences, first

Table 3
Kinetic parameters

Reactions	Rate constants (1/h)		
	RO of 1,3-DMCH on Ir/Al_2O_3-HD	RO of 1,2-DMCH on Ir/Al_2O_3-HD	RO of 1,2-DMCH on Ir/SiO_2-LD
cis-to-*trans*	29.3 ± 0.2	45.8 ± 0.6	16.0 ± 0.6
trans-to-*cis*	84.1 ± 0.6	13.3 ± 1.8	4.6 ± 1.8
cis-to-ring opening	3.5 ± 0.2	0.3 ± 0.1	1.4 ± 0.3
trans-to-ring opening	0.2 ± 0.1	5.1 ± 0.3	2.6 ± 0.3

Rate constants from fitting the experimental data in Figs. 12 and 13 with pseudo-first order kinetics.

note that dicarbene intermediates should be produced equally from *trans*- and *cis*-isomers for either reactant, because the substituents do not directly participate in formation of these intermediates; however, formation of the metallocycle intermediate will be greatly affected by steric hindrance and flexibility of the substituents. Accordingly, the higher reactivity of *cis*-1,3-DMCH and *trans*-1,2-DMCH is coincidental with the stability of the diequatorial conformers. Thus this conformation may be the most appropriate for generating the reaction intermediate that results in the opening of the substituted C–C bonds.

Although *cis*-1,2-DMCH exhibits hardly any ring opening activity on the Ir/Al_2O_3 catalyst, it is indeed able to react on Ir/SiO_2, as reflected by the relatively high rate constant. This result, together with the low $(a + b)/(c + d)$ ratio, indicates that both *cis*-1,2-DMCH and *trans*-1,3-DMCH react only via the dicarbene mode. In contrast, *cis*-1,3-DMCH and *trans*-1,2-DMCH can result in products with high CN (i.e., less branched).

5. Conclusion

Several conclusions can be drawn from this comparative study:

(i) It is possible to maximize the CN of a given feed of naphthenics by tailoring the catalyst and reaction conditions to maximize the ring opening at substituted C–C bonds, particularly those internal to the substituents. In contrast, if the desirable property to maximize is octane number, then the opposite trend should be chosen.

(ii) The predominant ring opening mechanism by direct hydrogenolysis of naphthenic C6 rings over Ir catalysts depends strongly on the type of support used and only slightly on the metal dispersion. On Ir/SiO_2 catalysts, the preferred reaction path is the dicarbene mode that cleaves C–C bonds at unsubstituted positions (secondary-secondary). This path results in products with high degrees of branching and, consequently, low CNs. Therefore, silica–supported catalysts with low metal dispersion would be useful in gasoline production. On Ir/Al_2O_3 catalysts, the metallocyclobutane mode becomes operative, leading to more desirable opening of substituted C–C bonds for products of high CN. The performance of the Ir/TiO_2 catalyst falls between that of the Ir/Al_2O_3 and Ir/SiO_2 catalysts.

(iii) The ratio between the high-CN products and low-CN products resulting from the substituted or unsubstituted C–C bond cleavage, respectively, decreases with conversion for all catalysts. This loss in CN with conversion is due to preferential hydrogenolysis of the longer chains on Ir. Therefore, a goal of future research is to find a catalyst with a high preference to substituted C–C bond cleavage but low activity for secondary hydrogenolysis of the primary products.

(iv) The presence of methyl substituents in the reactant molecule has a positive impact on the ring opening of substituted C–C bonds. The C–C bonds between methyl substituents are opened preferentially compared with those C–C bonds outside the methyl substituents. This preferential opening results in CN improvement.

(v) The predominant ring opening mechanism also depends on the molecular configuration, with different stereoisomers following different mechanisms. For instance, the ring opening of *cis*-1,3-DMCH and *trans*-1,2-DMCH proceeds via both metallocyclobutane and dicarbene mechanisms; in contrast, the other two isomers, *trans*-1,3-DMCH and *cis*-1,2-DMCH, can react only via the dicarbene mode.

Acknowledgments

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