

Ring opening of 1,3-dimethylcyclohexane on Ir catalysts Modification of product distribution by addition of Ni and K to improve fuel properties

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Abstract

The ring opening (RO) of 1,3-dimethylcyclohexane (DMCH) has been studied on a series of Ir catalysts. This molecule has been used as a model feed to compare catalysts that could be employed in the treatment of gasoline feedstocks for improving octane number (ON), while keeping low aromatics content and low vapor pressure. By changing the support and by adding promoters, we have been able to modify the product distribution and determine which catalyst modifications can be more effective. For example, Ir/SiO₂ catalyzes the opening of unsubstituted C–C bonds and yields products with a high degree of branching and consequently high ON. By contrast, Ir/Al₂O₃ is less selective and yields products with lower ON. This catalyst is at the same time more active and results in excessive secondary hydrogenolysis, producing increasing amounts of light-molecular weight products as the conversion increases. K and Ni were investigated as potential promoters to inhibit the secondary hydrogenolysis and make the Ir/Al₂O₃ catalyst more selective towards the cleavage of unsubstituted C–C bonds. It was found that while the addition of K decreased the secondary hydrogenolysis it did not change the ratio of substituted/unsubstituted C–C bond cleavage and had little effect in the resulting octane number of the product. By contrast, the addition of Ni was found to improve octane number without excessively increasing the vapor pressure of the mixture.

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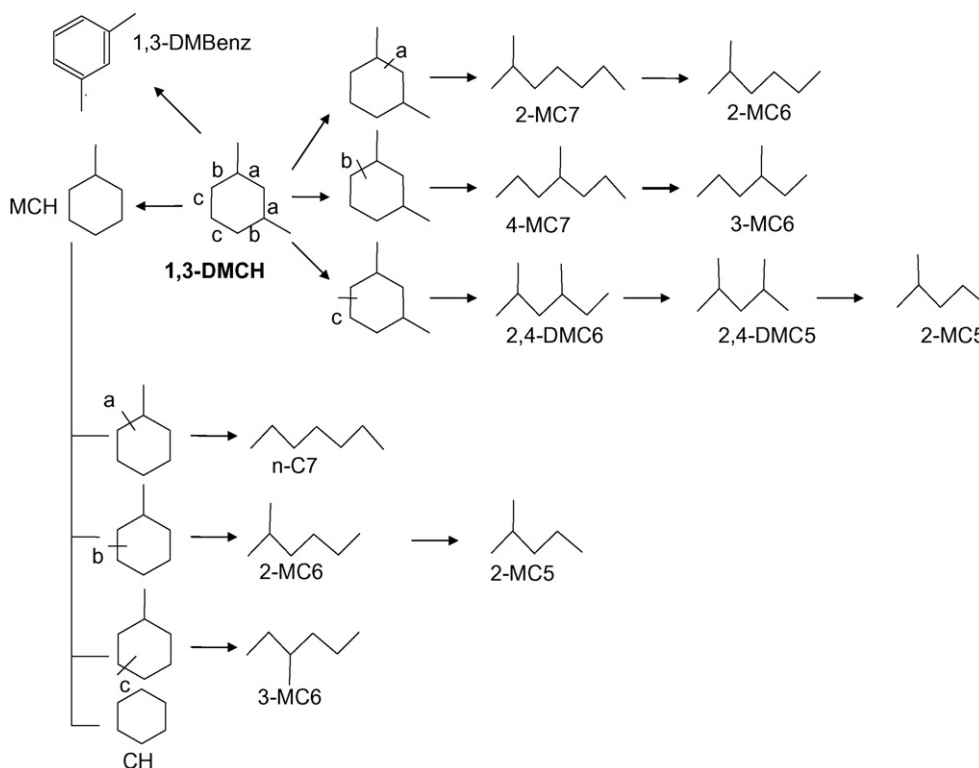
Keywords: Dimethylcyclohexane ring opening; Hydrogenolysis; Ir catalyst; Bimetallic catalysts; Fuel properties; Octane number

1. Introduction

Due to environmental concerns, new regulations call for reductions in aromatics contents in gasoline [1,2], which can be accomplished by hydrogenation. However, aromatic saturation results in octane number losses [3–5]. Octane number (ON) is defined in terms of the research octane number (RON), which represents engine operations typical of mild driving, and the motor octane number (MON), which represents severe, sustained high speed, high load driving. The pump octane number (ON) is the average between the two methods (RON + MON)/2.

To improve ON, a potential option is the selective ring opening (SRO) of the saturated naphthenes into paraffinic compounds with the same number of carbon atoms as the original molecules, but with a higher degree of branching. The loss of molecular weight of hydrocarbons during RO is undesirable since the presence of hydrocarbons with low molecular weight results in high Reid vapor pressure (RVP), which is strictly regulated to be less than 7.8 psi for gasoline mixtures in most parts of the United States. The concept of SRO of saturated naphthenic compounds, following deep hydrogenation of aromatics, was originally introduced to improve the cetane number of diesel fuel [6,7–11]. In that case, products with highly linear carbon chains, i.e. normal paraffins, are desirable due to their high CNs. On the other hand, *iso*-paraffins with a high degree of branching are preferred in gasoline since they have high ONs.

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Scheme 1. Some of the ring opening (primary) and hydrogenolysis (secondary) products obtained from 1,3-DMCH on Ir catalysts.

Opening of a naphthenic ring can be accomplished catalytically on either acidic or metallic catalysts. On an acidic catalyst, the C–C bond in the beta position from the *tertiary* carbon is favored to break [12]. Therefore, the corresponding products are branched, which makes acid catalysts a potential candidate for ON improvement. However, a drawback of acid catalysts is the excessive cracking to low-molecular weight products [13]. As first pointed out by Gault et al., ring opening of naphthenic compounds over metal catalysts can proceed via different mechanisms involving intermediates such as dicarbene, adsorbed olefin and metallocyclobutane [14,15]. The dicarbene mechanism results in the cleavage of unsubstituted C–C bonds, which retains the branches in the molecule. In the other two mechanisms, substituted C–C bonds are preferentially broken, which results in alkane products with less branching. Since the overall octane number can be greatly affected not only by the selectivity of the primary reaction (ring opening) but also by the subsequent hydrogenolysis of the primary products (see Scheme 1), we will compare the behavior of different catalysts at varying levels of conversion.

It is well established that the hydrogenolysis activity of Ir is one of the highest among catalytically active metals [16–19]. McVicker et al. have recently proposed to use Ir as an effective catalyst for the ring opening of six-member naphthenic rings [9]. They emphasized the tendency of Ir to favor the C–C bond cleavage via the dicarbene mode. In agreement with that study, we showed in our previous contribution [20] that the ring opening of two naphthenic molecules (1,2- and 1,3-dimethylcyclohexane) are indeed opened preferentially by the dicarbene mode, i.e. the ring opens at unsubstituted (secondary C–secondary C) posi-

tions. However, we found that the preference of C–C bond opening at unsubstituted positions compared to substituted ones (*tertiary*–*secondary* or *tertiary*–*tertiary*) depends rather strongly on the type of support used. While Ir on silica showed the expected preference for the dicarbene mode, Ir on alumina displayed an important selectivity towards ring opening at substituted C–C bonds. This selectivity was found to be a support effect rather than a particle size effect. Alumina-supported catalysts in a broad range of metal dispersions consistently showed higher selectivities to substituted C–C bond cleavage than any of the Ir catalysts supported on silica. It is not yet clear whether this dramatic support effect is due to the stabilization of specific metal cluster configurations or to the participation of specific sites on the oxide support present on alumina, but not on silica. Since metal dispersion does not seem to affect selectivity as much as the change in support, the stabilization of different cluster morphologies appears as a less likely explanation.

The dicarbene mode results in more highly branched products. Therefore, one may conclude that silica-supported Ir catalysts may be appropriate for generating ring opening products with high ON. However, the overall activity and stability of the silica-supported catalysts are rather low compared to alumina-support catalysts. It would be desirable to find a catalyst with the high activity and stability of the Ir/Al₂O₃ but with the selectivity to high ON products of Ir/SiO₂.

We attempt to find a possible solution by modifying alumina-supported catalysts with the addition of a second metal to Ir. In the first place, to inhibit the interaction between Ir and the alumina support, we have selected Ni as the additional metal. It is well known that Ni interacts strongly with alumina, forming sur-

face nickel aluminate-like species in the submonolayer regime [21]. Additionally, Ni and Ir can form solid solutions over the full range of concentrations, which may modify the catalytic behavior of Ir [22,23]. Another additive worth considering is potassium. It is well known that the presence of K can alter the catalytic activity and selectivity of metal catalysts due to both geometric and electronic effects [24,25,21].

In this contribution, we have focused on the ring opening of 1,3-dimethylcyclohexane (1,3-DMCH) over Ir catalysts modified by the addition of K and Ni. Particular attention was paid to the selectivity towards products of high octane number that keep the vapor pressure in the desirable range of gasolines.

2. Experimental

2.1. Materials investigated

Gamma-alumina (γ -Al₂O₃, HP-140 from Sasol) and silica (HiSil-210; PPG) were used as supports for the various catalysts investigated. All catalysts were prepared by incipient wetness impregnation (co-impregnation) with aqueous solutions of IrCl₃·3H₂O (Alfa-Aesar), NiCl₂·xH₂O (Alfa-Aesar), and K₂CO₃ (Alfa-Aesar). In each case, the concentration of the precursor solution was adjusted to the desired metal loading. In this study, a fixed metal loading of 0.9 wt.% Ir was used in the monometallic catalysts supported on Al₂O₃ and SiO₂ which are denoted as Ir/Al and Ir/SiO₂, respectively. For the bimetallic Ir-Ni catalysts, 0.3 and 0.1 wt.% Ni loadings were used in combination with 0.9 wt.% Ir on the Al₂O₃ support to obtain a Ni:Ir molar ratio of 1.0 and 0.3, respectively. The catalysts thus obtained are denoted as IrNi_{1.0}/Al₂O₃ and IrNi_{0.3}/Al₂O₃. In addition, sequential (two-step) impregnation was used to prepare a IrNi_{0.3}/Al₂O₃ catalyst; in this case, the calcined monometallic Ni/Al₂O₃ sample was further impregnated with the solution of the Ir precursor. For the 0.5 wt.% K-promoted catalysts, Al₂O₃ was impregnated with K before the impregnation with Ir, using a K concentration adjusted to a K:Ir molar ratio equal to 2.5 (IrK_{2.5}/Al₂O₃). After impregnation the samples were kept at ambient temperature for 4 h, then dried at 110 °C overnight, and finally calcined in air at 300 °C for the Ir and Ir-K catalysts, while a temperature of 400 °C was used for the Ir-Ni catalysts.

2.2. Catalyst characterization

Dynamic chemisorption of CO was used to estimate the metal dispersion on the different catalysts. The CO uptake measurements were performed in a 1/4" flow cell made of quartz, containing 0.1 g of sample. Before exposure to CO, the samples were reduced in situ under 50 ml/min of H₂ at 450 °C for 1 h, and purged in flowing He for 30 min and then cooled down to room temperature. The exit stream was continuously monitored by a mass spectrometer connected on line. After the pretreatment, calibrated pulses of 250 μ l of 5% CO in He were sent over the catalyst every 5 min, until the areas of the *m/e* = 28 peak stopped increasing, which indicated that the saturation adsorption capacity had been reached. The total amount of CO taken-up by the

sample was calculated by quantifying the area of the peak with the total number of CO moles present in the 250 μ l loop filled with 5% CO in He.

Temperature programmed reduction (TPR) on oxidized samples was carried out in a 1/4" quartz tube coupled to a thermal conductivity detector. A sample of 50 mg was heated in a flow of 20 cm³/min of 5.2% H₂ in Ar mixture, using a linear ramp of 10 °C/min up to 900 °C. Water produced during the reduction was removed using a cold trap of dry ice-acetone.

2.3. Catalytic activity measurements

The reactions of ring opening of 1,3-dimethylcyclohexane (1,3-DMCH, Sigma-Aldrich) and hydrogenolysis of two of the primary products (2,4-dimethylhexane, 2,4-DMC6, and 2-methylheptane, 2-MC7, from Sigma-Aldrich) were carried out on a fixed-bed reactor (1/2" OD stainless steel tube), equipped with a thermowell in the center of the catalysts bed to insert the thermocouple. The catalytic activity measurements were conducted in the gas phase at 330 °C, a H₂/HC molar ratio of 30, and a total pressure of 500 psig. The catalyst was first reduced for 1.5 h under flowing H₂ at 500 psig and 450 °C. After the pretreatment, the reactor was cooled down in flowing H₂. Then, the liquid reactant was introduced in the reactor using an Isco LC-500 high-pressure syringe pump. The products were collected in a dry-ice in acetone bath (at a temperature of 197 K to capture all the products) and were analyzed in a Hewlett Packard 5890 Plus GC and a Shimadzu GC-MS-P500.

3. Results and discussion

3.1. Characteristics of the catalysts investigated

The CO uptakes measured on the mono- and bimetallic catalysts are summarized in Table 1. From these values, it is clear that the Ir dispersion on Al₂O₃ is significantly higher than on SiO₂, as previously observed [26]. It is also seen that the addition of Ni or K on the alumina support results in a decrease in CO uptake.

The TPR profiles for the bimetallic Ir-Ni and monometallic Ir and Ni catalysts are illustrated in Fig. 1. The highly dispersed Ir/Al₂O₃ catalyst exhibited a single major peak with a maximum at about 200 °C, corresponding to the reduction of Ir oxide to metal Ir, as previously observed [27,28]. A monometallic Ni/Al₂O₃ sample was prepared for comparison; in this case two reduction peaks were observed, the first one at around 300 °C and a broad second one starting at 400 °C. Based on previous

Table 1
Compositions and metal dispersions of the 0.9 wt.% Ir-containing catalysts

Catalyst	Ni or K (wt. %)	Ni/Ir or K/Ir molar ratio	CO (μ mol/g)	CO/M ^a
Ir/Al ₂ O ₃	—	—	43.8	0.94
IrNi _{0.3} /Al ₂ O ₃	0.1	0.3	41.6	0.70
IrNi _{1.0} /Al ₂ O ₃	0.3	1.0	38.0	0.40
IrK _{2.5} /Al ₂ O ₃	0.5	2.5	35.0	0.75
Ir/SiO ₂	—	—	14.9	0.32

^a M is Ir or (Ir + Ni).

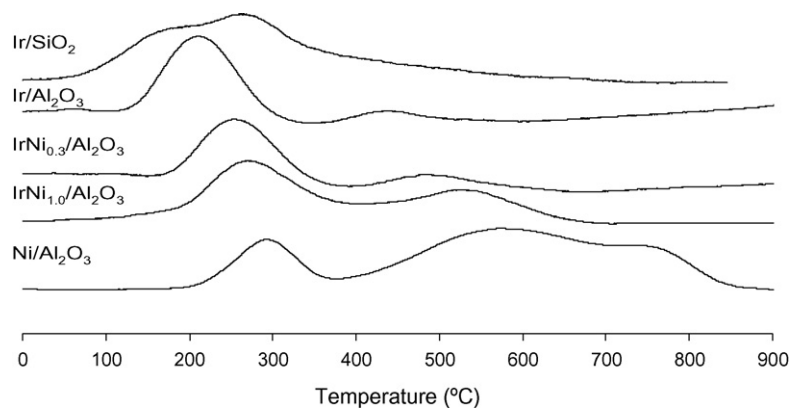


Fig. 1. Temperature programmed reduction of Ir, Ni and Ir–Ni catalysts.

Table 2a

Liquid product distribution obtained from 1,3-DMCH at 603 K, 3540 kPa, H₂/HC ratio of 30, and time on stream of 2 h over the different catalyst investigated (low conversion)

	Catalysts				
	Ir/Al ₂ O ₃	IrNi _{0.3} /Al ₂ O ₃	IrNi _{1.0} /Al ₂ O ₃	IrK _{2.5} /Al ₂ O ₃	Ir/SiO ₂
W/F (h)	0.025	0.06	0.13	0.12	0.30
Conversion (%)	2.9	3.5	3.5	19	15
C4–C5 (%)	–	0.15	0.35	0.9	0.5
2-MC5 (%)	0.08	0.04	0.03	0.3	0.3
3-MC5 (%)	–	–	–	0.03	0.1
CH (%)	–	–	–	0.01	–
2,4-DMC5 (%)	0.03	0.13	0.11	0.6	3.6
2-MC6 (%)	–	–	–	0.2	0.2
3-MC6 (%)	–	–	–	0.2	0.3
MCH (%)	0.2	0.12	0.15	0.8	0.6
2,4-DMC6 (%)	0.9	1.40	0.75	9.0	7.7
2-MC7 (%)	0.7	0.50	0.22	4.5	1.2
4-MC7 (%)	0.3	0.21	0.13	1.2	0.6
1,3-DMBenz (%)	0.6	0.9	1.8	0.8	0.6

reports, the first peak corresponds to the reduction of Ni oxide while the second peak is due to the reduction of highly interacting Ni oxide in a surface-aluminate phase, which strongly inhibits the reducibility of Ni [22,29–31]. As previously demon-

strated for other bimetallic systems [32–34], TPR is an excellent technique to quantify the degree of metal-metal interaction and even predict in a semi-quantitative form the distribution of relative concentrations when the reducibility of the two components

Table 2b

Liquid product distribution obtained from 1,3-DMCH at 603 K, 3540 kPa, H₂/HC ratio of 30, and time on stream of 2 h over the different catalyst investigated (high conversion)

	Catalysts				
	Ir/Al ₂ O ₃	IrNi _{0.3} /Al ₂ O ₃	IrNi _{1.0} /Al ₂ O ₃	IrK _{2.5} /Al ₂ O ₃	Ir/SiO ₂
W/F (h)	0.20	0.25	0.33	0.33	0.82
Conversion (%)	39.5	28	75	55	41
C4–C5 (%)	3.2	1.20	69	6	1.3
2-MC5 (%)	1.3	0.5	0.03	3.4	1.3
3-MC5 (%)	0.11	0.06	–	0.4	0.5
CH _x (%)	0.04	–	–	0.1	0.05
2,4-DMC5 (%)	1.7	2.5	0.4	4.6	11.3
2-MC6 (%)	0.06	0.3	0.01	1.6	0.8
3-MC6 (%)	1	0.3	0.03	1.8	1.3
MCH (%)	2.3	0.6	0.6	0.9	1.5
2,4-DMC6 (%)	18.2	13.8	1.7	23	19.3
2-MC7 (%)	8.3	3.3	0.5	10	2.3
4-MC7 (%)	2.5	0.9	–	3.1	1
1,3-DMBenz (%)	0.9	4.3	2.9	0.3	0.5

is significantly different, as in the present case of Ni and Ir. In this case, it is clear that the first peak for the two IrNi/Al₂O₃ catalysts appears in the intermediate region between those corresponding to the reduction of Ir and Ni. This intermediate position suggests that both oxides are in intimate contact since the reduction of Ir is delayed by the interaction with Ni and, at the same time, Ir acts as a catalyst to help the reduction of Ni.

The Ir/SiO₂ catalyst has a significantly lower dispersion and may have a broader distribution of particle sizes. The shoulder observed at 180 °C in addition to the main peak at 290 °C may reflect the presence of iridium oxides species with different degrees of aggregation [35,36].

In summary, the characterization of the different catalysts investigated demonstrates that the series contains a wide variety of metal dispersions, metal/support, metal–metal, and metal–additive interactions. This is therefore an interesting series of Ir-based catalysts that allow us to compare the effect of these parameters on the product distribution, and consequently on the desired fuel properties.

3.2. Ring opening (RO) of 1,3-DMCH on monometallic Ir catalysts

Tables 2a and 2b summarize the product distribution obtained at a time on stream of 2 h over the different catalysts investigated. The three primary products, 2-methylheptane (2-MC7), 4-methylheptane (4-MC7) and 2,4-dimethylhexane (2,4-DMC6), dominate at low conversions. As previously reported [20], the silica-supported Ir catalyst predominantly opens the ring on secondary C–secondary C bonds (dicarbene mechanism), while the alumina-supported Ir catalyst also opens the substituted C–C bonds. As the conversion increases, these primary products are further cracked to 2,4-dimethylpentane (2,4-DMC5), 2-methylhexane (2-MC6), 3-methylhexane (3-MC6), 2-methylpentane (2-MC5), 3-methylpentane (3-MC5), 2-methylbutane (2-MC4), *iso*-butane (*iso*-C4), and *n*-butane (*n*-C4). As shown in Tables 2a and 2b the distribution of these secondary products varies from catalyst to catalyst as well as with the conversion level. This variation opens the opportunity of finding the conditions that maximize octane number while keeping the vapor pressure below acceptable limits.

For this analysis, we have summarized in Fig. 2 the octane numbers (ON defined as the average between RON and MON) and vapor pressure (VP) of all RO products. It can be seen that only five products, 2,4-DMC6, 2,4-DMC5, 2-MC5, 3-MC5 and 2-MC4, have ON higher than the ON = 63 of the original feed. Therefore, we will focus on maximizing the yield of these five products, denoted as HON products. Although the ON of 2-MC4 is also high (ON = 90), it will not be considered in this group due to its high vapor pressure. The evolution of the total yield of these HON products was followed as a function of W/F for the monometallic Ir/Al₂O₃ and Ir/SiO₂ catalysts (see Fig. 3a). Due to the higher activity of alumina-supported Ir catalysts, mentioned in our previous work [20], the Ir/Al₂O₃ catalyst is seen to yield at low W/F higher amounts of HON products than the Ir/SiO₂ catalyst. However, as W/F increases, the primary products continue to break into lighter products (<C5), which results

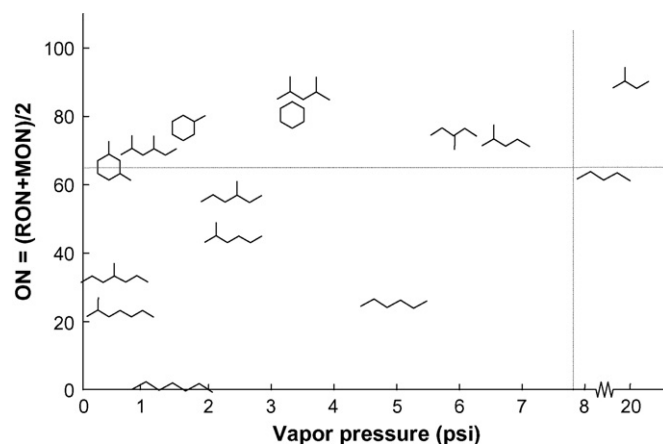


Fig. 2. Octane number and vapor pressure of typical products of 1,3-DMCH ring opening.

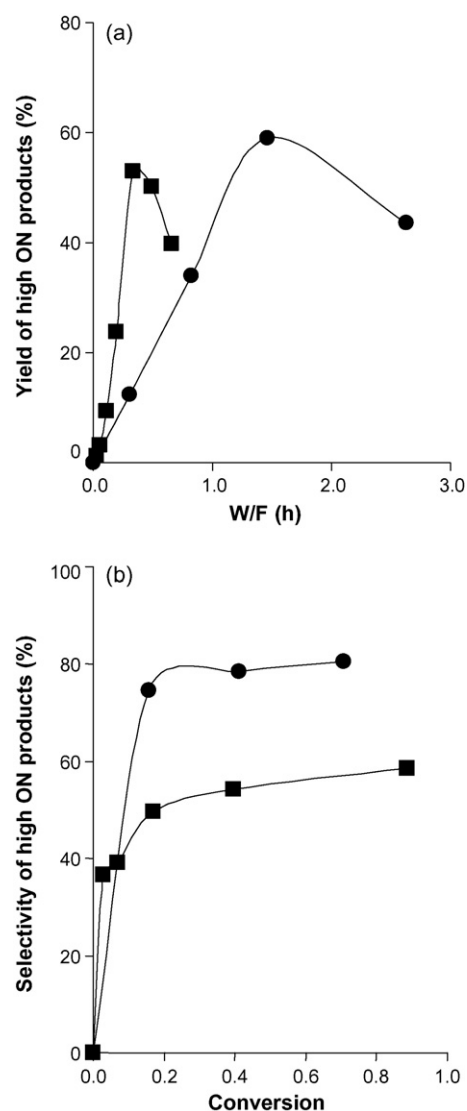


Fig. 3. (a) Yield of high Octane number products (HON, 2,4-DMC6, 2,4-DMC5, 2-MC5, 3-MC5) from ring opening of 1,3-DMCH. Reaction was conducted at 603 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. (■) Ir/Al₂O₃; (●) Ir/SiO₂. (b) Selectivity of high Octane number products (HON, 2,4-DMC6, 2,4-DMC5, 2-MC5, 3-MC5).

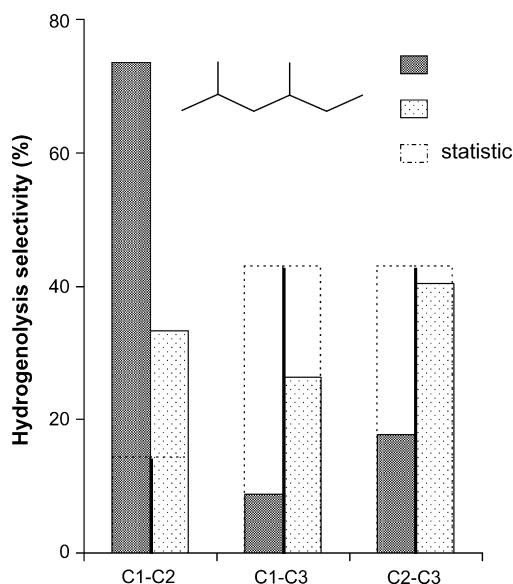


Fig. 4. Selectivities of hydrogenolysis of 2,4-DMC6 at different C–C bond positions. Reaction was conducted at 603 K and 3540 kPa. Hydrogen and hydrocarbon ratio was kept at 30, whsv = 0.008 h on Ir/Al₂O₃ and 0.025 h on Ir/SiO₂. Products 2,4-DMC5 (from C1 to C2); 3-MC6 and 2-MC6 (from C1 to C3); 2-MC5, *iso*-C4, and *iso*-C5 (from C2 to C3).

in a decrease in the total yield of HON products for both catalysts. As shown below, the selectivity of this secondary reaction greatly varies from catalyst to catalyst. Although ring opening activity of Ir/Al₂O₃ is higher than that of Ir/SiO₂, selectivity toward high octane number products on Ir/SiO₂ is significantly high compared to Ir/Al₂O₃ as illustrated in Fig. 3b.

Since the hydrogenolysis reaction of primary and secondary products to lighter molecules is important in the resulting ON and vapor pressure of the product mixture, the secondary hydrogenolysis of 2-MC7 and 2,4-DMC6 was tested separately in order to better understand the effect of support and molecular structure on product distribution. Figs. 4 and 5 show the hydrogenolysis product pattern of these two hydrocarbons on Ir/Al₂O₃ and Ir/SiO₂ catalysts. To facilitate the analysis and to focus on the intrinsic selectivity toward specific C–C bond cleavages, the reaction conversion was kept below 5%. The hydrogenolysis of 2,4-DMC6 and 2-MC7 yields six and seven products, respectively, which corresponds to cleavage of different C–C bonds in the molecules. In the case of 2,4-DMC6, there are three different groups of bonds, primary–secondary (C1–C2), primary–*tertiary* (C1–C3) and secondary–*tertiary* (C2–C3). For the other molecule investigated, 2-MC7, there is an additional type of bond, the secondary–secondary (C2–C2). The selectivities for different bond cleavages are compared in Figs. 4 and 5 with the corresponding statistical values. Several interesting trends can be identified. In the first place, in agreement with the differences previously observed [20], it is seen that in the case of 2,4-DMC6, the preference for the cleavage of the unsubstituted C1–C2 bond compared to substituted C–C bonds is much more pronounced on Ir/SiO₂ than on Ir/Al₂O₃. In fact, the latter generates products of substituted C–C bond cleavage closer to the statistical than the former. By contrast, in the case of 2-MC7, the differences in product distribution between the

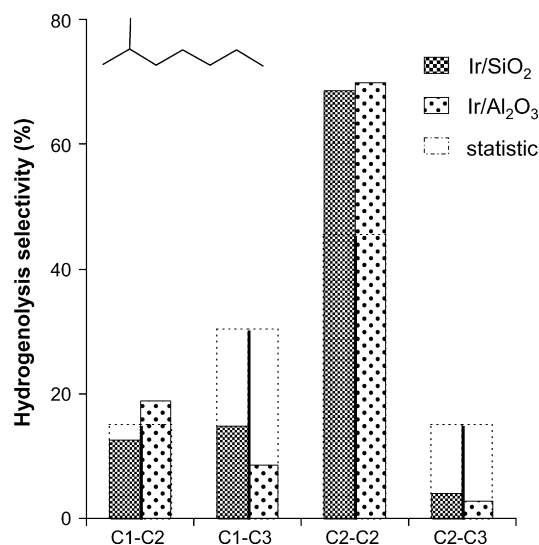


Fig. 5. Selectivities of hydrogenolysis of 2-MC7 at different C–C bond positions. Reaction was conducted at 603 K and 3540 kPa. Hydrogen and hydrocarbon ratio was kept at 30, whsv = 0.008 h on Ir/Al₂O₃ and 0.025 h on Ir/SiO₂. Products 2-MC6 (from C1 to C2); *n*-C7 (from C1 to C3); 2-MC5, 2-MC4, *iso*-C4, and *n*-C4 (from C2 to C2); *n*-C5 (from C2 to C3).

two catalysts are very small and, in this case, both catalysts seem to prefer the dicarbene route, with the C2–C2 cleavage as the dominant reaction path, which according to previous studies, is the one of lowest activation energy [37].

From the analysis of the secondary product evolution, we can better understand the evolution of the HON products of the 1,3-DMCH feed shown in Fig. 6(a) and (c) as a function of W/F for the alumina- and silica-supported catalysts, respectively. At low W/F, 2,4-DMC6 is the dominant product for both catalysts. However, as the conversion increases, the primary products are cracked to lower-carbon-number molecules. Interestingly, the evolution of the secondary product 2,4-DMC5 as a function of W/F is very different from one catalyst to another. On the Ir/Al₂O₃ catalyst, it starts to accumulate slowly, reaches a maximum and then rapidly drops. By contrast, on the Ir/SiO₂ catalyst, it increases more rapidly and drops more slowly. The reason for the more rapid increase on the silica-supported catalyst can be found in Fig. 4; the terminal cracking that converts 2,4-DMC6 into 2,4-DMC5 is much preferred on the Ir/SiO₂ catalyst. At the same time, 2,4-DMC5 only contains substituted C–C bonds, whose cleavage is unfavorable on the silica-supported catalyst. Therefore, this molecule is not converted fast on this catalyst. As a result, the maximum yield of 2,4-DMC5 reaches 22% on Ir/SiO₂ but only 10% on Ir/Al₂O₃. As discussed below, this difference has an impact on the resulting ON, since 2,4-DMC5 is one of the products with the highest ON.

The selectivity of HON of 1,3-DMCH as a function of conversion on Ir/Al₂O₃ and Ir/SiO₂ is illustrated in Fig. 6(b) and (d), respectively. At low conversion, selectivity of 2,4-DMC6 significantly increases with increase in conversion, then slightly decreases at higher conversions on both catalysts, due to the influence of secondary hydrogenolysis of the primary products. In contrast, the secondary products (2,4-DMC5, 2-MC5, and 3-MC5) continuously increase as a function of conversion.

3.3. Reactions on bimetallic Ni–Ir catalysts

To capitalize some of the advantages of the alumina support but avoiding the excessive loss of HON products by extensive hydrogenolysis, we have explored modifying both the support and the metal particles by adding Ni as a potential additive. It is well known that Ni is capable of blocking the interaction between noble metals and alumina by forming aluminate-like surface species in the submonolayer regime [21]. Additionally, alloys between Ni and noble metals are widely reported as a way of modifying the selectivity. In the present work, we have tested two Ir–Ni catalysts with varying molar ratios (Ir:Ni = 1:1 and 1:0.3). The sample with a higher Ni content, i.e. IrNi_{1.0}/Al₂O₃, showed a catalytic behavior typical of Ni [38,39]; that is, de-methylation was the only reaction observed,

as opposed to the desired ring opening products. By contrast, the IrNi_{0.3}/Al₂O₃ sample showed the behavior of a modified Ir catalyst. As depicted in Fig. 6(e), the presence of Ni resulted in a significant change in product evolution in comparison to the monometallic Ir/Al₂O₃ catalyst. Both the faster appearance of the secondary product (2,4-DMC5) and the slower drop in concentration of 2,4-DMC6 and 2,4-DMC5 are characteristics which are closer to the behavior of Ir/SiO₂ than to that of Ir/Al₂O₃. That is, the fast over-conversion found on the Ir/Al₂O₃ catalyst was prevented by the addition of Ni. In addition, it is clearly shown in Fig. 6(f), that the selectivity towards 2,4-DMC6 and 2,4-DMC5 is much higher on IrNi_{0.3}/Al₂O₃ than on Ir/Al₂O₃ (as shown in Fig. 6(b)). That is, by a tailoring the addition of an additive such as Ni one could be able to maximize the desired products by modify-

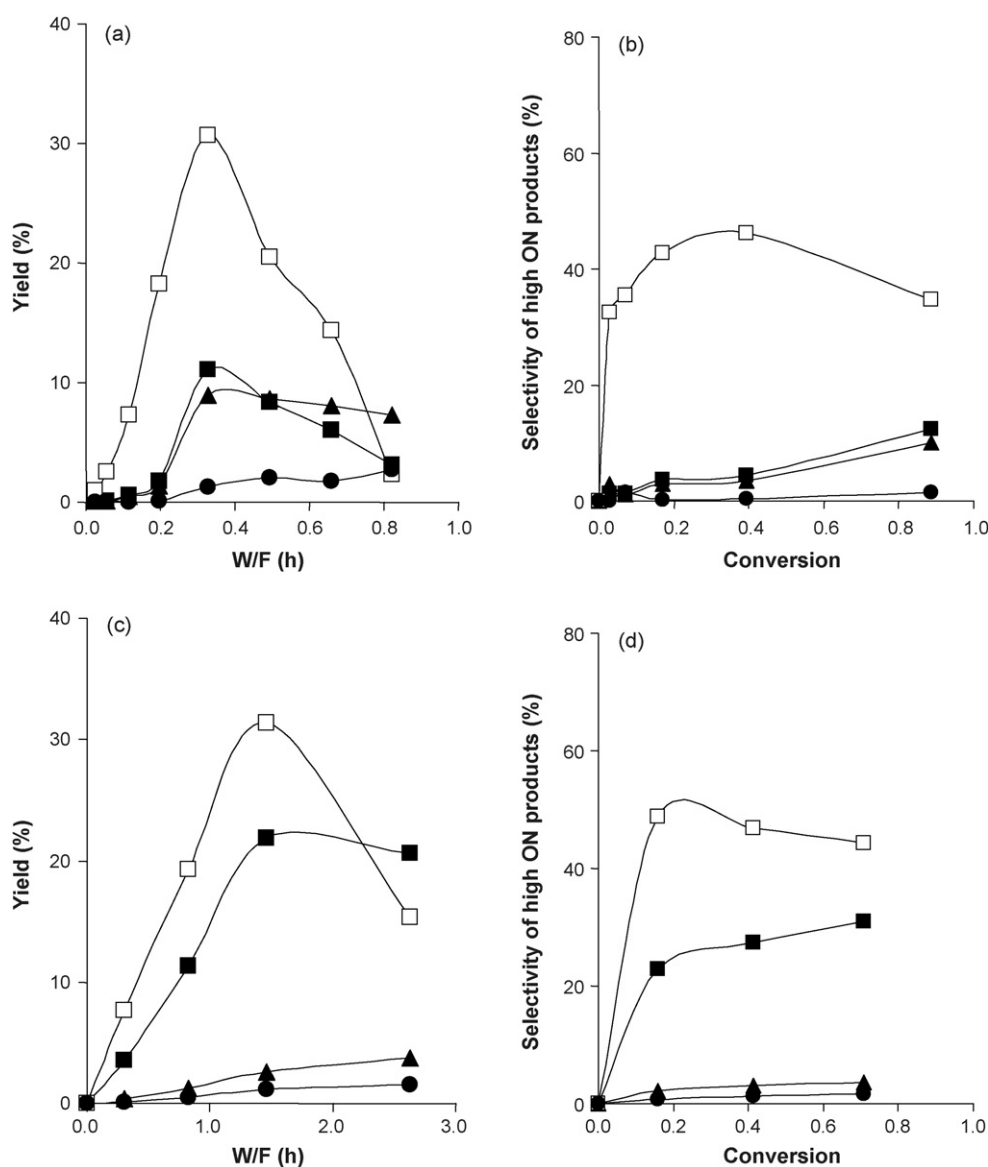


Fig. 6. (a) Yield of high Octane number products from ring opening of 1,3-DMCH over Ir/Al₂O₃ catalyst. (b) Selectivity. (c) Yield of high Octane number products from ring opening of 1,3-DMCH over Ir/SiO₂ catalyst. (d) Selectivity. (e) Yield of high Octane number products from ring opening of 1,3-DMCH over IrNi_{0.3}/Al₂O₃ catalyst. (f) Selectivity. (g) Yield of high octane number products from ring opening of 1,3-DMCH over IrK_{2.5}/Al₂O₃ catalyst. (h) Selectivity. In all cases, reaction conducted at 603 K and 3540 kPa; H₂ to hydrocarbon ratio was kept at 30. (□) 2,4-DMC6; (■) 2,4-DMC5; (▲) 2-MC5; (●) 3-MC5.

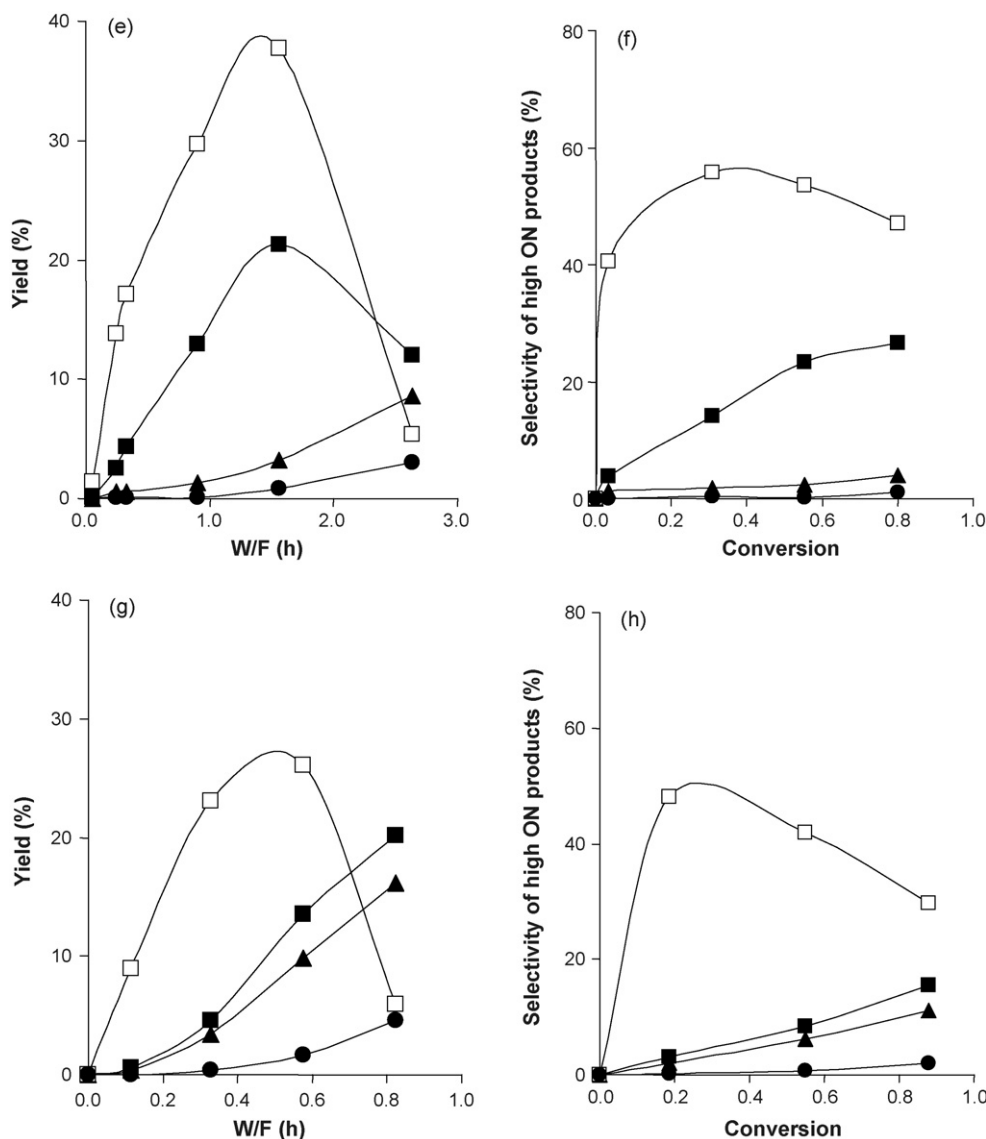


Fig. 6. (Continued).

ing the selectivity in the desired direction while keeping high activity.

While it is certainly possible that the intrinsic catalytic behavior of Ir may be affected by alloying with Ni, it is conceivable that the aluminate species formed during the calcination step inhibit the interaction of Ir with the alumina. As shown in our previous work [20], we attribute the formation of the metallocyclobutane intermediate required to break the substituted C–C bonds, to special Ir sites adjacent to the alumina surface. The interaction of Ni with alumina might block this type of sites. Fig. 6(e) shows that the Ni-containing catalyst preferentially produces 2,4-DMC6 (from primary RO) and 2,4DMC5 (from secondary hydrogenolysis). Since both products result from C–C cleavage at unsubstituted positions (dicarbene) and this is typical of silica-supported Ir, we could say that the Ni-promoted catalyst behaves more like Ir/SiO₂ than like Ir/Al₂O₃.

3.4. Reactions on K-promoted Ir catalysts

It is well known that the presence of alkali additives can alter both the catalytic activity and selectivity of noble metal catalysts. In this case, we have investigated a K-doped Ir catalyst, IrK_{2.5}/Al₂O₃, with K/Ir molar ratios of 2.5. As shown in Table 1, the addition of K caused a modest decrease in the fraction of Ir exposed, which resulted in a drop in activity compared to that of the Ir/Al₂O₃ catalyst. The most important difference between the K-promoted and the unpromoted Ir/Al₂O₃ catalysts was that the former was able to maintain a much higher yield of the secondary products 2,4-DMC5 and 2-MC5. This is due to an inhibition by K in the conversion of the secondary products. By comparing Fig. 6(a) and (g), we can see that while 2,4-DMC6 starts decreasing at about the same W/F over the two catalysts, 2,4-DMC5 and 2-MC5 keep increasing on the K-promoted catalyst. The selectivity of HON as a function of conversion on IrK_{2.5}/Al₂O₃ is

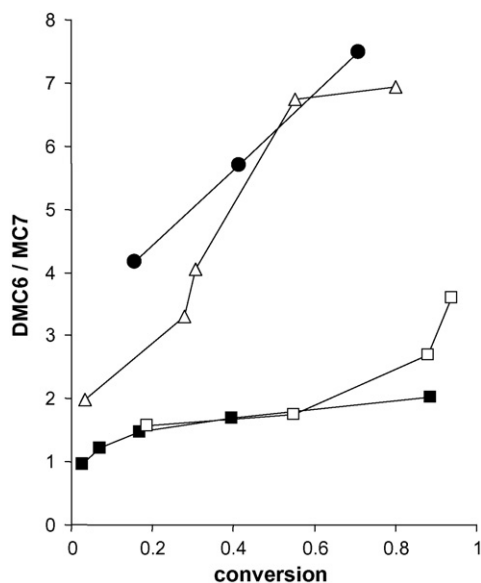


Fig. 7. Ratio of di-branched to mono-branched C8 products from 1,3-DMCH ring opening as a function of total conversion. Reaction conducted at 603 K to 3540 kPa; H₂ to hydrocarbon ratio was kept at 30. Catalysts: (■) Ir/Al₂O₃; (●) Ir/SiO₂; (△) IrNi_{0.3}/Al₂O₃; (□) IrK_{2.5}/Al₂O₃.

also illustrated in Fig. 6(h). The addition of K results in a profile similar to that observed on un-promoted Ir/Al₂O₃ (Fig. 6(b)).

Fig. 7 illustrates the different behavior of the various catalysts investigated in reference to the substituted or unsubstituted C–C bond cleavage. A measure of the relative rate of these two types of C–C cleavage is the ratio between the dibranched and monobranched products. The former arises from ring opening at unsubstituted positions, leaving the number of branches unchanged, while the latter arises from cleaving substituted C–C bonds, which eliminates one of the branches. As previously shown, Ir/SiO₂ preferentially opens unsubstituted C–C bonds via dicarbene intermediates [9,20]. By contrast, Ir/Al₂O₃ opens all the bonds in a more uniform distribution. Interestingly, while the K-promoted catalyst IrK_{2.5}/Al₂O₃ retains the behavior of an alumina-supported catalyst, the Ni-promoted catalyst (IrNi_{0.3}/Al₂O₃) behaves more like the silica-supported one.

3.5. Impact of the ring opening and hydrogenolysis reactions on octane number (ON) and Vapor Pressure of the product mixture

To obtain the ON of the product mixture we have used a model recently developed by Ghosh et al. [40] that uses the ON and molar compositions of the individual compounds combined with interaction coefficients for each type of molecules, alkanes and naphthenes in this case. The naphthenes are the unreacted cis and trans 1,3-DMCH. The alkanes include RO and hydrogenolysis products from C5 to C8. By using this model, the octane number of the product mixture was calculated as a function of W/F for the different catalysts investigated. The vapor pressures of the product mixtures at 37.8 °C (100 °F), temperature at which the Reid Vapor Pressure is typically measured, were calculated by using Pro II 7.0 software, from SimSci–Esscor.

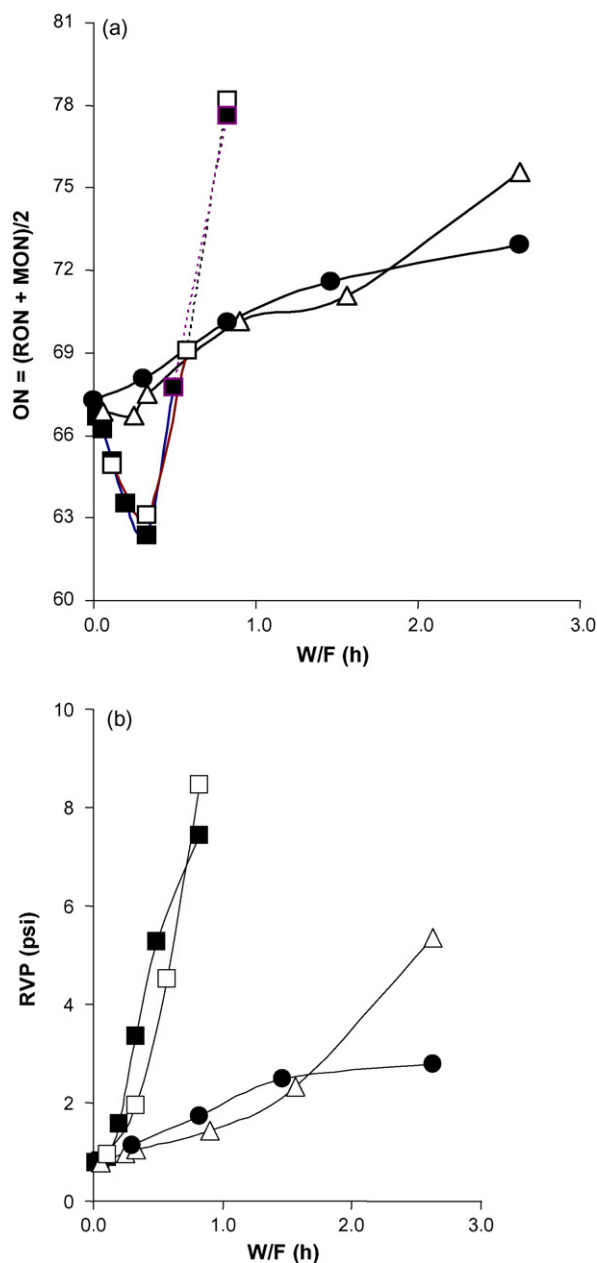


Fig. 8. (a) Octane number of product mixture from ring opening of 1,3-DMCH, calculated by method of Ref. [40]. (b) Reid vapor pressure (RVP) of product mixture from ring opening of 1,3-DMCH. Reaction was conducted at 603 K and 3540 kPa. Hydrogen to hydrocarbon ratio was kept at 30. (■) Ir/Al₂O₃; (●) Ir/SiO₂; (△) IrNi_{0.3}/Al₂O₃; (□) IrK_{2.5}/Al₂O₃.

As shown in Fig. 8(a), two different trends are observed. For the Ir/Al₂O₃ and IrK_{2.5}/Al₂O₃ catalysts, the ON of the product initially decreases with W/F, but after a given bed length, it starts increasing rapidly. The initial drop in ON can be explained in terms of the primary RO products. On the alumina-supported catalyst, the RO at substituted positions is relatively high and this type of RO yields products of low ON (e.g. 2-MC7: ON = 23; 4-MC7: ON = 33). Only after the secondary hydrogenolysis starts generating significant amounts of shorter-chain products (i.e. at about W/F = 0.3) the ON starts increasing. However, as depicted in Fig. 8(b), this rapid increase in ON is accom-

panied by an equally rapid increase in vapor pressure of the mixture.

A very different trend was obtained on the Ir/SiO₂ and IrNi_{0.3}/Al₂O₃ catalysts, for which the ON continuously increased as a function of W/F. On these catalysts, cleavage of the unsubstituted C–C bonds is strongly preferred. As a result, not only the concentration of primary products of low ON (2-MC7 and 4-MC7) is low, but also the production of 2,4-DMC5 via terminal bond (C1–C2) hydrogenolysis of 2,4-DMC6 is high. The direct consequence is a continuous increase in ON with W/F. At the same time, the lower activity of these two catalysts for the extensive hydrogenolysis reduces the production of lighter products, and as a result, the increase in the RVP vapor pressure. As mentioned above, the stronger similarity of IrNi_{0.3}/Al₂O₃ with Ir/SiO₂ rather than with Ir/Al₂O₃ may be ascribed to the formation of a surface Ni-aluminate that may act as a barrier between Ir and the alumina support.

4. Conclusions

The addition of K to the Ir/Al₂O₃ catalyst results in decreased secondary hydrogenolysis, but does not affect the ratio of substituted to unsubstituted ring opening. As a result, the increase in octane number is not much different from that obtained on the Ir/Al₂O₃ catalyst. By contrast, the addition of Ni to Ir/Al₂O₃ catalyst at appropriate molar ratios suppresses the cleavage of C–C bond at substituted positions, thus making the alumina-supported catalyst behave more like a silica-supported catalyst, giving a product with improved octane number and moderate vapor pressure.

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References

- [1] W.J. Petzny, C.-P. Halsig, Proceedings of the DGMK Conference on The Future Role of Aromatics in Refining and Petrochemistry, Erlangen, Germany, October 13–15, 1999, pp. 7–20.
- [2] K. Owen, T. Coley, Automotive Fuels Reference Book, 2nd ed., Soc. Autom. Engin. Inc., Warrendale, PA, 1995.

- [3] J. Weitkamp, A. Raichle, Y. Traa, M. Rupp, F. Fuder, Chem. Commun. 1133 (2000).
- [4] A. Raichle, Y. Traa, F. Fuder, M. Rupp, J. Weitkamp, Angew. Chem. Int. Ed. 40 (2001) 1243.
- [5] J. Wang, Q. Li, J. Yao, Appl. Catal. A 184 (1999) 181.
- [6] D. Kubička, N. Kumar, P.M. Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi, D.Y. Murzin, J. Catal. 227 (2004) 313.
- [7] M.A. Arribas, P. Concepción, A. Martínez, Appl. Catal. A 267 (2004) 111.
- [8] A. Corma, V. González-Alfaro, A.V. Orchillés, J. Catal. 200 (2001) 200.
- [9] G.B. McVicker, M. Daage, M.S. Touvelle, C.W. Hudson, D.P. Klein, W.C. Baird, B.R. Cook, J.G. Chen, S. Hantzer, D.E.W. Vaughan, E.S. Ellis, O.C. Feeley, J. Catal. 210 (2002) 137.
- [10] D. Kubička, N. Kumar, P.M. Arvela, M. Tiitta, V. Niemi, T. Salmi, D.Y. Murzin, J. Catal. 222 (2004) 65.
- [11] R.C. Santana, P.T. Do, M. Santikunaporn, W.E. Alvarez, J.D. Taylor, E.L. Sughrue, D.E. Resasco, Fuel 85 (2006) 643.
- [12] M. Santikunaporn, J.E. Herrera, S. Jongpatiwut, D.E. Resasco, W.E. Alvarez, E.L. Sughrue, J. Catal. 228 (2004) 100.
- [13] D.G. Blackmond, J.G. Goodwin, J.E. Lester, J. Catal. 78 (1982) 34.
- [14] G. Maire, G. Plouidy, J.C. Prudhomme, F.G. Gault, J. Catal. 4 (1965) 556.
- [15] F.G. Gault, Advances in Catalysis, vol. 30, Academic Press, 1981, p. 1.
- [16] T.J. Plunkett, J.K.A. Clark, J. Catal. 35 (1974) 330.
- [17] Z. Karpinski, J.K.A. Clarke, J. Chem. Soc. Faraday Trans. 171 (1975) 2310.
- [18] J.H. Sinfelt, Catal. Rev. 3 (1969) 175.
- [19] M. Boudart, L.D. Ptak, J. Catal. 16 (1970) 90.
- [20] T. Do Phuong, W.E. Alvarez, D.E. Resasco, J. Catal. 238 (2006) 477.
- [21] T. Osaki, T. Mori, J. Catal. 204 (2001) 89.
- [22] V. Boissel, S. Tahir, C.A. Koh, Appl. Catal. B 64 (2006) 234.
- [23] T. Abbas, F.A. Khawaja, Solid State Commun. 49 (1984) 641.
- [24] A.A. Balandin, in: D.D. Eley, W.G. Frankenburg, V.I. Komarewsky, P.B. Weisz (Eds.), Advances in Catalysis, vol. 10, Academic Press, 1958, p. 96.
- [25] D.A. Dowden, J. Chem. Soc. 242 (1950).
- [26] J.M. Guil, A.P. Masiá, A.R. Paniago, J.M.T. Menayo, Thermochim. Acta 312 (1998) 115.
- [27] Y.-J. Huang, S.C. Fung, W.E. Gates, G.B. McVicker, J. Catal. 118 (1989) 192.
- [28] S. Subramanian, J.A. Schwarz, Appl. Catal. 74 (1991) 65.
- [29] T. Osaki, T. Horiuchi, T. Sugiyama, K. Suzuki, T. Mori, Catal. Lett. 52 (1998) 71.
- [30] J. Zieliliski, J. Mol. Catal. 83 (1993) 197.
- [31] J. Wang, L. Dong, Y. Hu, G. Zheng, Z. Hu, Y. Chen, J. Catal. 204 (2001) 274.
- [32] G.M. Nuñez, A.J. Rouco, J. Catal. 111 (1988) 41.
- [33] F.M. Dautzenberg, J.N. Helle, P. Biloen, W.M.H. Sachtler, J. Catal. 63 (1980) 119.
- [34] S.D. Robertson, B.D. Mcnicol, J.H. De Baas, S.C. Kloet, J.W. Jenkins, J. Catal. 37 (1975) 424.
- [35] K. Fogar, H. Jaeger, J. Catal. 70 (1981) 53.
- [36] C. Wögerbauer, M. Maciejewski, A. Baiker, U. Göbel, J. Catal. 201 (2001) 113.
- [37] K. Fogar, J.R. Anderson, J. Catal. 59 (1979) 325.
- [38] G. Leclercq, L. Leclercq, L.M. Bouleau, S. Pietrzyk, R. Maurel, J. Catal. 88 (1984) 8.
- [39] H. Du, C. Fairbridge, H. Yang, Z. Ring, Appl. Catal. A 294 (2005) 1.
- [40] P. Ghosh, K.J. Hickey, S.B. Jaffe, Ind. Eng. Chem. Res. 45 (2006) 337.