CHAPTER VI
RING OPENING OF 1,3-DIMETHYLCYCLOHEXANE ON Ir CATALYSTS. MODIFICATIN OF PRODUCT DISTRIBUTION BY ADDITION OF Ni AND K TO IMPROVE FUEL PROPERTIES*

6.1 Abstract

The ring opening (RO) of 1,3-dimethylcyclohexane (1,3-DMCH) was studied on a series of Ir catalysts. The 1,3-DMCH was used as a modeled feed to compare catalysts that could be employed in the treatment of gasoline feedstocks for improving octane number (ON), whereby keeping low aromatics content and low vapor pressure. By changing the support and the addition of promoters, we have been able to modify the product distribution. For example, Ir/SiO_2 catalyzes the opening of unsubstituted C-C bonds and yields products with high degree of branching and consequently high ON. In contrast, Ir/Al_2O_3 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 reduce the secondary hydrogenolysis and make the Ir/Al_2O_3 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 products. In contrast, the addition of Ni was found to modify both improving octane number and without excessively increasing the vapor pressure of the mixture.

6.2 Introduction

Due to environmental concerns, new regulations call for reductions in aromatics content in both gasoline and diesel [1-2]. For diesel fuel, hydrogenation of aromatics to saturated naphthenes results in increasing cetane number (CN), which is desirable. In contrast, for gasoline, aromatics 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 selective ring opening (SRO) of the saturated naphthenes into paraffinic compounds with the same number of carbon atoms as the original molecules, but with higher degrees of branching. The loss of molecular weight of hydrocarbons during ring opening is undesirable since the presence of hydrocarbons with low moleclar 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 [6-11]. In that case, products with highly linear carbon chains, i.e normal paraffins, are desirable due to their high cetane numbers. On the other hand, iso-paraffins with a high degree of branching are preferred in gasoline since they have high octane numbers.

Opening of naphthenic rings 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 was favored to break [12]. Therefore, the corresponding products were branched, which make acid catalysts a potential candidate for ON improvement. However, a drawback of acid catalysts was 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 could proceed via different mechanisms involving intermediates such as dicarbene, adsorbed olefins or

metallocyclobutane [14-15]. The dicarbene mechanism resulted in the cleavage of unsubstituted C-C bonds, which retains the branches in the molecule. In the other two mechanisms, substituted C-C bonds were preferentially broken, which resulted in alkane products with higher linearity. 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 6.1), we will compare the behavior of different catalysts at varying levels of conversion.
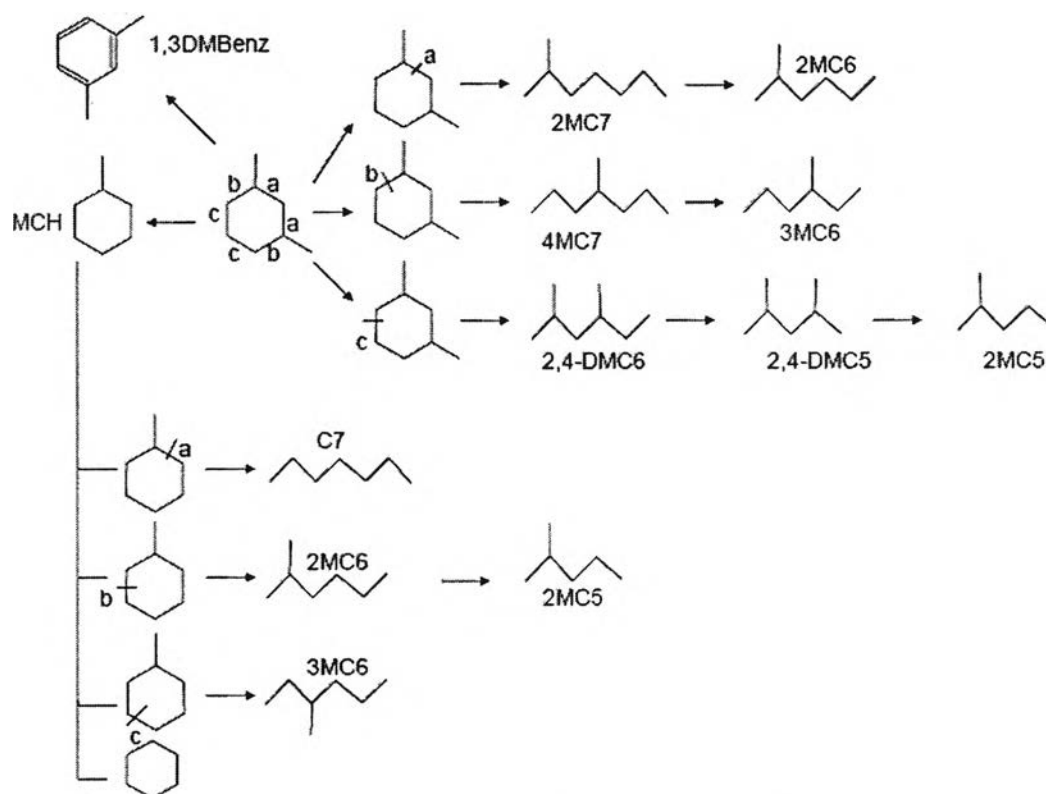
Scheme 6.1 Some of the ring opening (primary) and hydrogenolysis (secondary) products obtained from 1,3-DMCH on Ir catalysts.

It is well established that the hydrogenolysis activity of Ir stands out among all catalytically active metals [16-19]. McVicker *et al.* have recently called attention to the use of 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) positions. However, we found that the preference of C–C bond opening at unsubstituted positions compared to substituted positions (tertiary-secondary or tertiary-tertiary) depends rather strongly on the type of support used. While Ir on silica showed the expected preference for 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 particle size effect. Alumina-supported catalysts with different metal dispersions showed higher selectivities to substituted C-C bond cleavage than any of the catalysts supported on silica.

Since the dicarbene mode results in more highly branched products, therefore, one may conclude that the silica-supported Ir catalyst may be appropriate for generating ring opening products with high octane number. However, the overall activity and stability of the silicasupported catalysts are rather low as compared to alumina-support catalysts. It would be desirable to find a catalyst with the high activity and stability of the Ir/Al_2O_3 but with the selectivity to high ON products of Ir/SiO_2.

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 surface 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 behaviour 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 [24-26].

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, whereby keeping the vapor pressure in the desirable range of gasoline.

6.3 Experimental

6.3.1 Materials Investigated

Gamma-alumina (γ-Al_2O_3, 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 $IrCl_3.3H_2O$ (Alfa-Aesar), $NiCl_2.xH_2O$ (Alfa-Aesar), and K_2CO_3 (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 Al_2O_3 and SiO_2. 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 Al_2O_3 support to obtain a Ni:Ir molar ratio of 1.0 and 0.3, respectively. The catalysts thus obtained are denoted as $IrNi_{1.0}/Al_2O_3$ and $IrNi_{0.3}/Al_2O_3$, respectively. In addition, sequential (two-step) impregnation was used to prepare an IrNi0.3/Al2O3 catalyst; in this case, a calcined monometallic 0.1wt % Ni/Al2O3 sample was further impregnated with the solution of the Ir precursor. For the K-promoted catalysts, 0.5 wt.% K was impregnated on Al_2O_3, before the impregnation with Ir, using a K concentration adjusted to obtain a K:Ir molar ratio equal to 2.5 (0.9Ir-0.5K/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 whereas a temperature of 400°C was used for the Ir-Ni catalysts.

6.3.2 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" OD 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 H_2 at 723 K 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 µl 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 µl loop filled with 5%CO in He.

Temperature programmed reduction (TPR) on oxidized samples was carried out in a 1/4" OD quartz tube coupled with a thermal conductivity detector. A sample of 50 mg was heated in a flow of 20 cm^3/min of 5.2% H_2 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.

6.3.3 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-methlyheptane (2-MC7), from Sigma-Aldrich) were carried out in a fixed bed reactor (1/2" OD stainless steel tube), equipped with a thermowell at the center of the catalysts bed to insert a thermocouple. The catalytic activity measurements were conducted in gas phase at 603 K, a H_2/HC molar ratio of 30, and a total pressure of 3504 kPa. The catalyst was first reduced for 1.5 h under flowing H_2 at 3504 kPa and 723 K. After the pretreatment, the reactor was cooled down in flowing H_2. 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 contained acetone bath (at a temperature of 197 K to capture all the products) and were analyzed using a Hewlett Packard 5890 Plus GC and a Shimadzu GC-MS-P500.

6.4 Results and Discussion

6.4.1 Characteristics of the Catalysts Investigated

The CO uptakes measured on the mono and bimetallic catalysts are summarized in Table 6.1. From these values, it is clear that the Ir dispersion on Al_2O_3 is significantly higher than that on SiO_2, as previously observed [27]. Also, it is seen that the addition of Ni or K on the alumina support results in a decrease in CO uptake.

Table 6.1 Composition and metal dispersions of the 0.9 wt.% Ir-containing catalysts

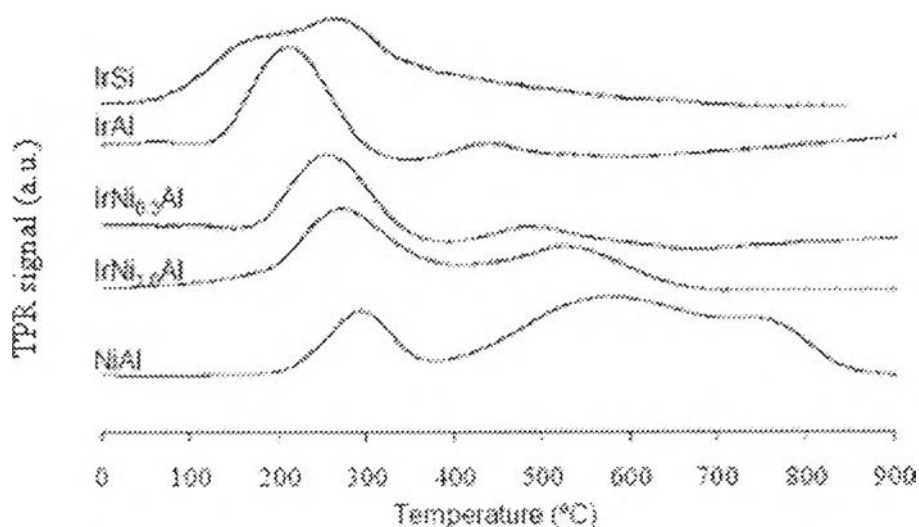| Catalyst	Loading (wt.%) Ni or K	Ni/Ir or K/Ir molar ratio	CO (μmol/g)	CO/M[a]
Ir/Al_2O_3	-	-	43.8	0.94
$IrNi_{0.3}/Al_2O_3$	0.1	0.3	41.6	0.70
$IrNi_{1.0}/Al_2O_3$	0.3	1.0	38.0	0.40
$IrK_{2.5}/Al_2O_3$	0.5	2.5	35.0	0.75
Ir/SiO_2	-	-	14.9	0.32

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

Figure 6.1 Temperature programmed profiles for reduction of Ir, Ni and IrNi on various support catalysts.

The TPR profiles for the bimetallic IrNi and monometallic Ir and Ni catalysts are illustrated in Figure 6.1. The highly dispersed Ir/Al_2O_3 catalyst exhibites a single major peak with a maximum at about 200 °C, corresponding to the reduction of Ir oxide to metal Ir, as previously observed [28, 29]. A monometallic Ni/Al_2O_3 sample was prepared for comparison; in this case two reduction peaks are observed, the first one at around 300 °C and, the second one as a broad increase in consumption starting at 400 °C. Based on previous 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 [30- 32]. The profiles of the two monometallic samples can be used to interpret the profiles of the bimetallic catalysts. It is clear that the first peaks for the two $IrNi/Al_2O_3$ catalysts present in the intermediate region between those corresponding to the reduction of Ir and Ni are observed. As previously demonstrated for other bimetallic systems [33] this intermediate position suggests that both oxides be in intimate contact; 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/SiO_2 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 [34-35].

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 will allow us to compare the effect of these parameters on the product distribution, and consequently on the desired fuel properties.

6.4.2 Ring Opening of 1,3-DMCH on Monometallic Ir Catalysts

Tables 6.2a and 6.2b summarize the product distribution obtained at a time on stream of 2 hours 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 opened the ring on secondary C-

secondary C bonds (dicarbene mechanism), while the alumina-supported Ir catalyst also opened the substituted C-C bonds. As a 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 6.2a and 6.2b 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.

Table 6.2a Liquid product distribution from 1,3-DMCH at 603 K, 3540 kPa, H_2/HC ratio of 30, and time on stream of 2 hours over the different catalysts investigated (low conversion)

Catalysts / Products	IrAl	IrNi$_{0.3}$Al	IrNi$_{1.0}$Al	IrK$_{2.5}$Al	IrSi
W/F (h)*	0.025	0.06	0.13	0.12	0.30
conversion	2.9%	3.5%	3.5%	19.0%	15%
C4-C4	-	0.15%	0.35%	0.9%	0.5%
2MC5	0.08%	0.04%	0.03%	0.3%	0.3%
3MC5	0.60%	-	-	0.03%	0.1%
CHx	-	-	-	0.01%	-
2,4-DMC5	-	0.13%	0.11%	0.6%	3.6%
2MC6	0.03%	-	-	0.2%	0.2%
3MC6	-	-	-	0.2%	0.3%
MCH	-	0.12%	0.15%	0.8%	0.6%
2,4-DMC6	0.20%	1.40%	0.75%	9.0%	7.7%
2MC7	0.90%	0.50%	0.22%	4.5%	1.2%
4MC7	0.70%	0.21%	0.13%	1.2%	0.6%
1,3-DMenz	0.30%	0.9%	1.8%	0.8%	0.6%

* vol$_{cat}$*h/vol

Table 6.2b Liquid product distribution from 1,3-DMCH at 603 K, 3540 kPa, H_2/HC ratio of 30, and time on stream of 2 hours over the different catalysts investigated (high conversion)

Catalysts / Products	IrAl	$IrNi_{0.3}Al$	$IrNi_{1.0}Al$	$IrK_{2.5}Al$	IrSi
W/F*	0.2	0.25	0.33	0.33	0.82
conversion	39.5%	28.0%	75.0%	55.0%	41.0%
C4-C4	3.2%	1.20%	69%	6.0%	1.3%
2MC5	1.3%	0.50%	0.03%	3.4%	1.3%
3MC5	0.11%	0.06%	-	0.4%	0.5%
CHx	0.04%	-	-	0.1%	0.05
2,4-DMC5	1.7%	2.5%	0.4%	4.6%	11.3%
2MC6	0.06%	0.3%	0.01%	1.6%	0.8%
3MC6	1.0%	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%	23.0%	19.3%
2MC7	8.3%	3.3%	0.5%	10.0%	2.3%
4MC7	2.5%	0.9%	-	3.1%	1.0%
1,3-DMenz	0.9%	4.3%	2.9%	0.3%	0.5%

* vol_{cat}*h/vol

For this analysis, we have summarized in Figure 6.2 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 sum of yield of the other four HON products was followed as a function of W/F for the monometallic Ir/Al$_2$O$_3$ and Ir/SiO$_2$ catalysts (see Figure 6.3). Due to the higher activity of alumina-supported Ir catalysts, mentioned in our previous work [20] the Ir/Al$_2$O$_3$ catalyst is seen to yield at low W/F higher amounts of HON products than the Ir/SiO$_2$ catalyst. However, as a W/F ratio increases, the primary products continue to break into lighter products (<C5), resulting in a decrease in the sum of yield of HON products for both catalysts. As shown in Figure 6.3, the selectivity of this secondary reaction greatly varies from catalyst to catalyst.
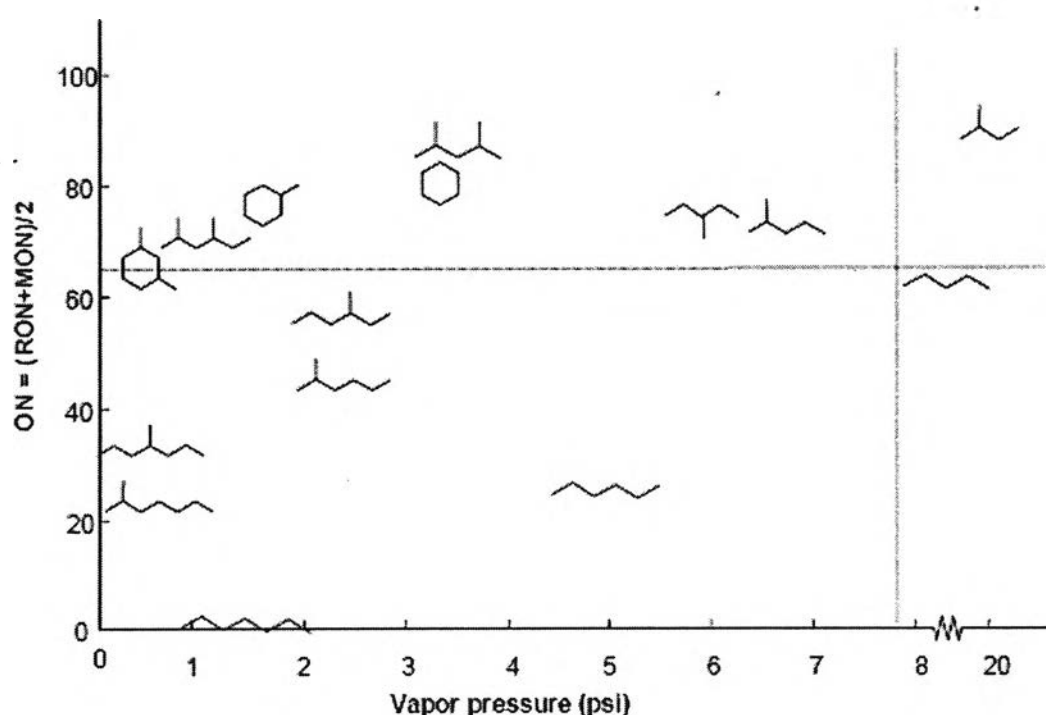

Figure 6.2 Octane number and vapor pressure of typical products of 1,3-DMCH ring opening.
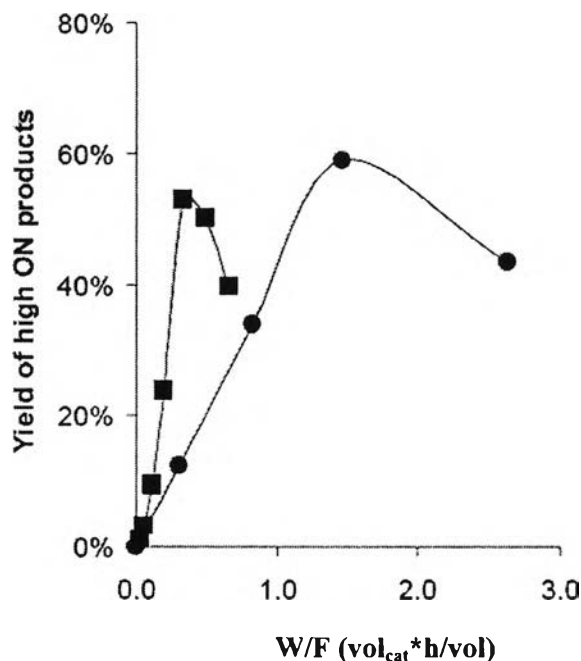
Figure 6.3 Yield of high octane number products (2,4-DMC6, 2,4-DMC5, 2MC5, 3MC5) on Ir/Al₂O₃ (■) and Ir/SiO₂ (●)catalysts.

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. Figures 6.4 and 6.5 show the hydrogenolysis product pattern of these two hydrocarbons on Ir/Al₂O₃ and Ir/SiO₂ catalysts. To facilitate the analysis and 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 yield 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 selectivity for different bond cleavages are compared in Figures 6.4 and 6.5 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/SiO$_2$ than on Ir/Al$_2$O$_3$. 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 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 [36].
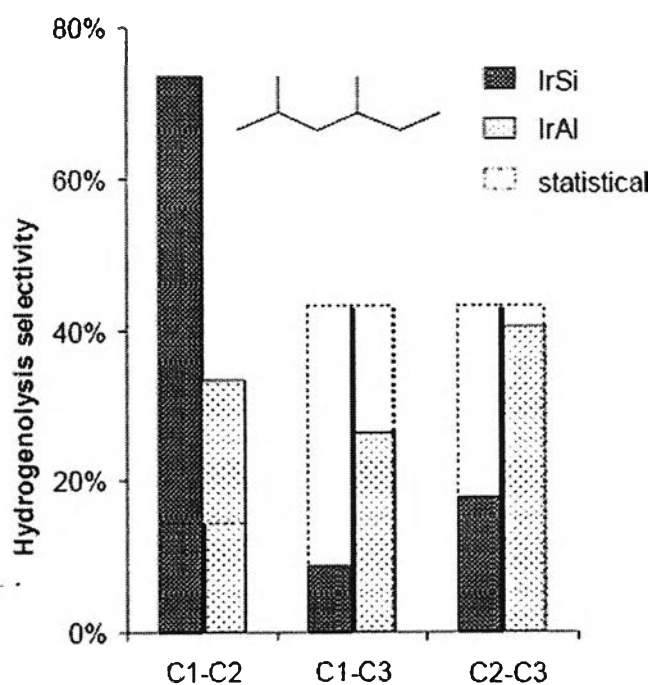
Figure 6.4 Selectivities of hydrogenolysis of 2,4-DMC6 at different C-C bond position was conducted at 603 K and 3540 kPa. H$_2$/HC ratio of 30, whsv of 0.008 h on Ir/Al$_2$O$_3$ and 0.025 h on Ir/SiO$_2$. Products 2,4-DMC5 (from C1-C2); 3-MC6 and 2MC6 (from C1-C3); 2-MC5, iso-C4 and iso-C5 (from C2-C3).
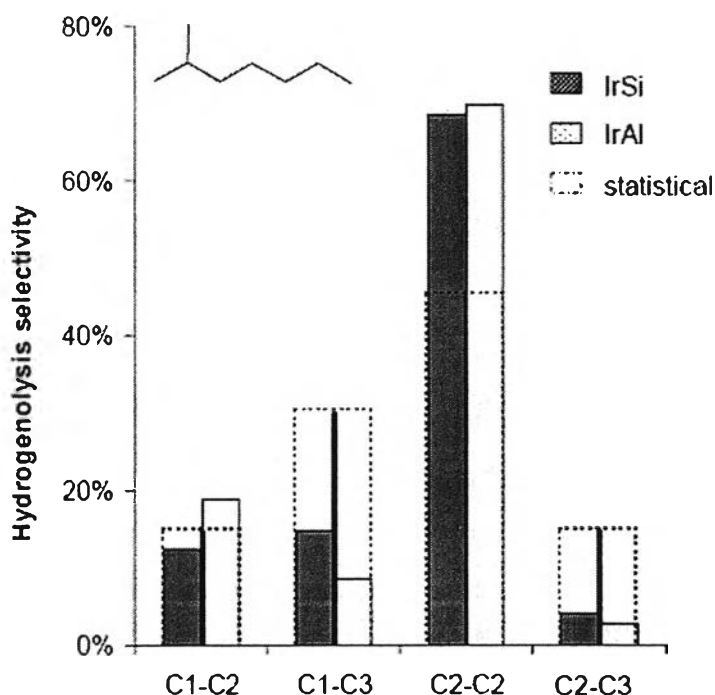
Figure 6.5 Selectivities of hydrogenolysis of 2-DMC7 at different C-C bond position was conducted at 603 K and 3540 kPa. H_2/HC ratio of 30, whsv of 0.008 h on Ir/Al_2O_3 and 0.025 h on Ir/SiO_2. Products 2,4-DMC5 (from C1-C2); 3-MC6 and 2MC6 (from C1-C3); 2-MC5, iso-C4 and iso-C5 (from C2-C3).

From this analysis of the secondary product evolution, we can better understand the evolution of the HON products of the 1,3-DMCH feed shown in Figs. 6.6a and 6.6b 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/Al_2O_3 catalyst, it starts to accumulate slowly, reaches a maximum and then rapidly drops.
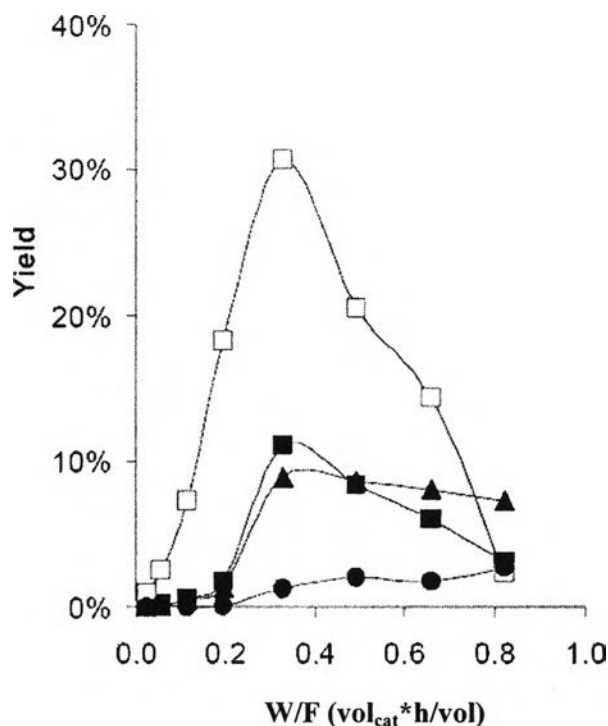
Figure 6.6a Yield of high octane number products from ring opening of 1,3-DMCH over Ir/Al$_2$O$_3$ catalyst. Reaction was conducted at 603 K and 3540 kPa, H$_2$/HC ratio of 30. □, 2,4-DMC6; ■ , 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.

In contrast, on the Ir/SiO$_2$ catalyst, it increases more rapidly and disappears a much less faster. The reason for the more rapid increase on the silica-supported catalyst can be found in Figure 6.4, the terminal cracking that converts 2,4-DMC6 into 2,4-DMC5 is much preferred on the Ir/SiO$_2$ catalyst. At the same time, 2,4-DMC5 only contains substituted C-C bonds, whose cleavage is unfavourable on the silica-supported catalyst. Therefore, this molecule is not converted as fast on this catalyst. As a result, the maximum yield of 2,4-DMC5 reaches 22% on Ir/SiO$_2$ but only 10 % on Ir/Al$_2$O$_3$. 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.
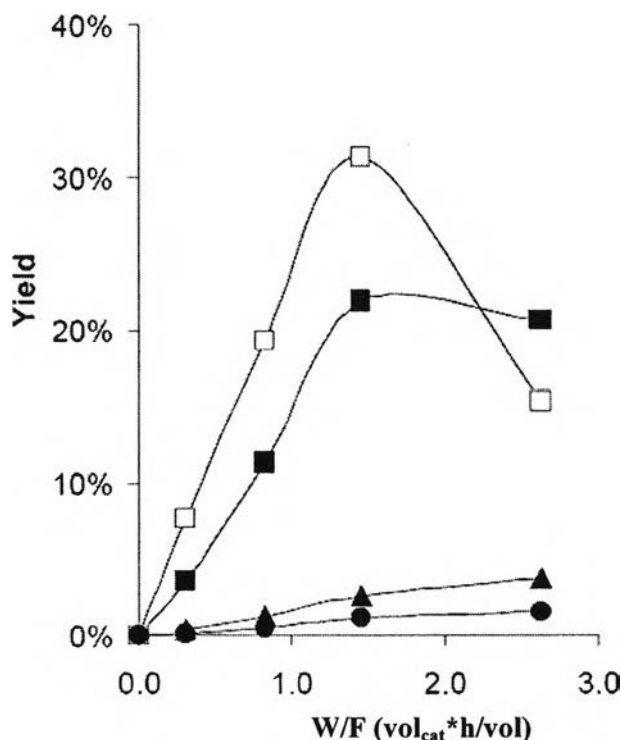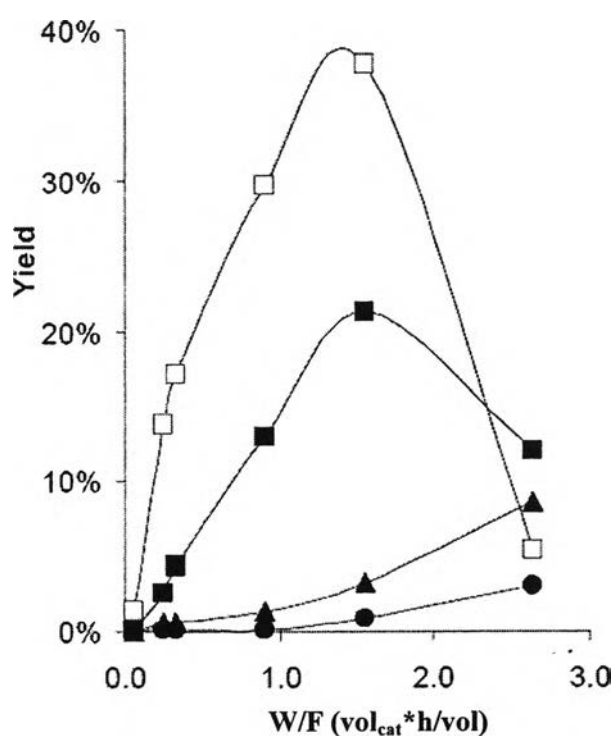
Figure 6.6b Yield of high octane number products from ring opening of 1,3-DMCH over Ir/SiO$_2$ catalyst. Reaction was conducted at 603 K and 3540 kPa, H$_2$/HC ratio of 30. □, 2,4-DMC6; ■, 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.

6.4.3 Reactions on Bimetallic Ni-Ir Catalysts

To take advantage of 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 higher Ni content, i.e. IrNi1.0/Al$_2$O$_3$, showed a catalytic behavior typical of Ni [37-38] that is, de-methylation was the only reaction observed, as opposed to the desired ring opening products. In contrast, the IrNi$_{0.3}$/Al$_2$O$_3$ sample showed the behavior of a modified Ir catalyst. As depicted in Figure 6.6c, the

presence of Ni resulted in a significant change in product evolution in comparison to the monometallic Ir/Al$_2$O$_3$ catalyst. Both the faster appearance of the secondary product (2,4-DMC5) and the delay in the W/F needed for start losing 2,4- DMC6 and 2,4-DMC5 are characteristics which are closer to the behavior of Ir/SiO$_2$ than to that of Ir/Al$_2$O$_3$. That is, the fast over-conversion found on the Ir/Al$_2$O$_3$ catalyst was prevented by the addition of Ni.

Figure 6.6c Yield of high octane number products from ring opening of 1,3-DMCH over IrNi$_{0.3}$Al catalyst. Reaction was conducted at 603 K and 3540 kPa, H$_2$/HC ratio of 30. □, 2,4-DMC6; ■ , 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.

It is conceivable that the aluminate species formed during the calcination step inhibit the interaction of Ir with the alumina resulting in a lower Ir dispersion. Most importantly, 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 interaction. Figure 6.6c 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/SiO_2 than like Ir/Al_2O_3.

6.4.4 Reactions on K-Promoted Ir Catalyst

It is well known that the presence of alkali additives can alter both the catalytic activity and selectivity of noble metal catalysts.
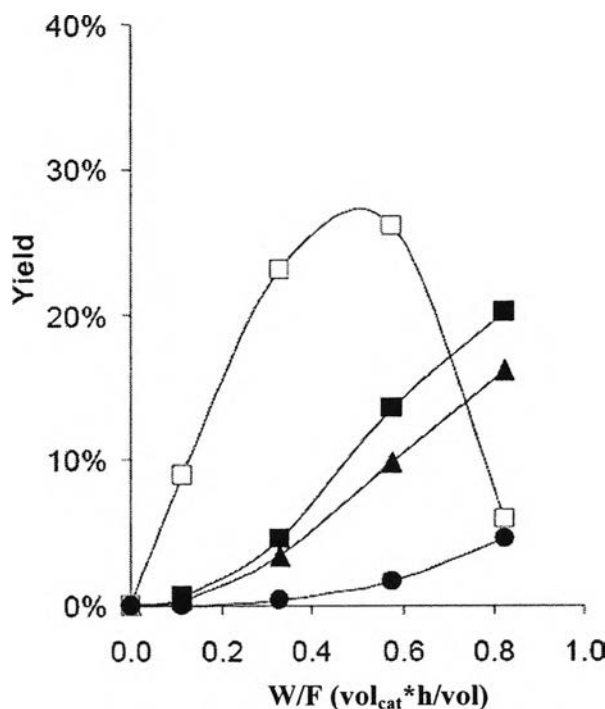

Figure 6.6d Yield of high octane number products from ring opening of 1,3-DMCH over IrKAl catalyst. Reaction was conducted at 603 K and 3540 kPa, H_2/HC ratio of 30. □, 2,4-DMC6; ■, 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.

In this case, we have investigated K doped Ir catalysts, $IrK_{2.5}/Al_2O_3$ with a K/Ir molar ratio of 2.5. As shown in Table 6.1, 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/Al_2O_3 catalyst. The most important difference between the K-promoted and the unpromoted Ir/Al_2O_3 catalysts was that the former was able to maintain a 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 Figures 6.6a and 6.6d, we can see that while 2,4-DMC6 start decreasing at about the same W/F over the two catalysts, 2,4-DMC5 and 2-MC5 keep increasing on the K-promoted catalyst.
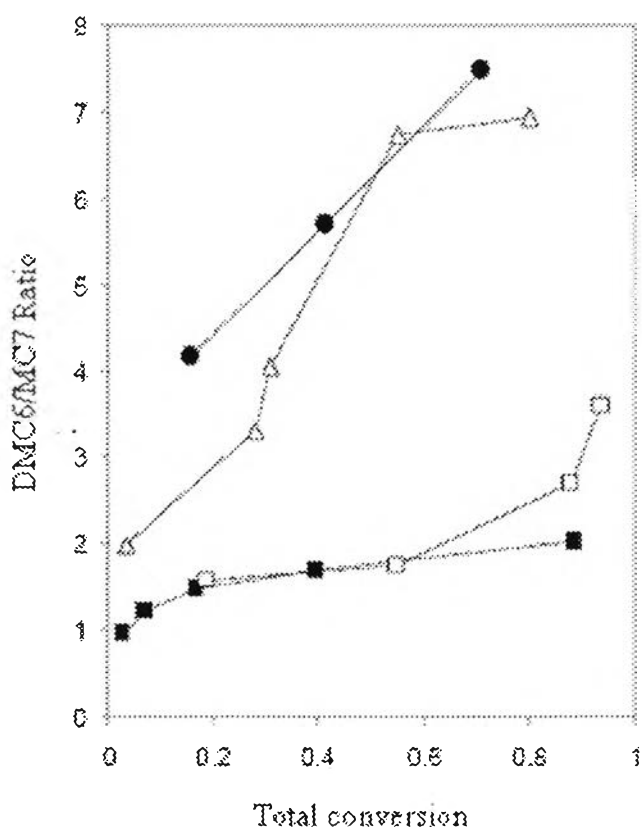

Figure 6.7 Ratio of di-branched to mono-branched C8 products from 1,3-DMCH ring opening as a function of total conversion. Reaction conducted at 603 K and 3540 kPa, H_2/HC ratio of 30. Catalysts: ■, IrAl; ●, IrSi; △ IrNi0.3Al; □, IrK2.5Al.

Figure 6.7 illustrates the different behaviour 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/SiO_2 preferentially opens unsubstituted C-C bonds via dicarbene intermediates [9, 20]. By contrast, Ir/Al_2O_3 opens all the bonds in a more uniform distribution. Interestingly, while the K-promoted catalyst $IrK_{2.5}/Al_2O_3$ retains the behavior of an alumina-supported catalyst, the Ni-promoted catalyst ($IrNi_{0.3}/Al_2O_3$) behaves more like the silica-supported one.

6.4.5 Impact of the Ring Opening and Hydrogenolysis Reactions on Octane Number and Ried Vapor Pressure of the Product Mixture

To obtain the octane number (ON) of the product mixture we have used a model recently developed by Ghosh *et al.* [39] 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 1,3DMCH. 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.

As shown in Figure 6.8, two different trends are observed. For the Ir/Al_2O_3 and $IrK_{2.5}/Al_2O_3$ 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. 2MC7: ON = 23; 4MC7: 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 Figure 6.9, this rapid increase in ON is accompanied by an equally rapid increase in vapor pressure of the mixture. The Reid vapor pressures (RVP) of the product mixtures were calculated by using Pro II 7.0 software, from SimSci-Esscor.
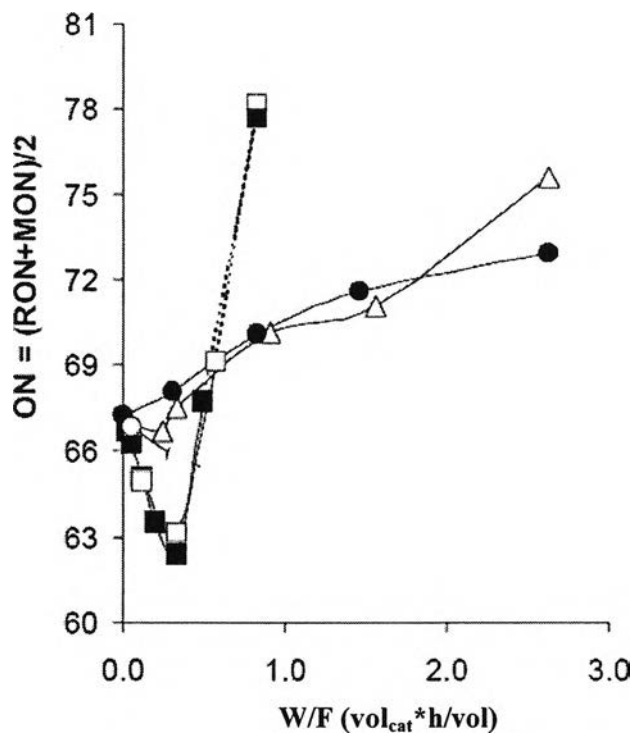
Figure 6.8 Octane number of product mixture from ring opening of 1,3-DMCH, calculated by method of Ref. [38]. ■, IrAl; ●, IrSi; △ IrNi0.3Al; □, IrK2.5Al.
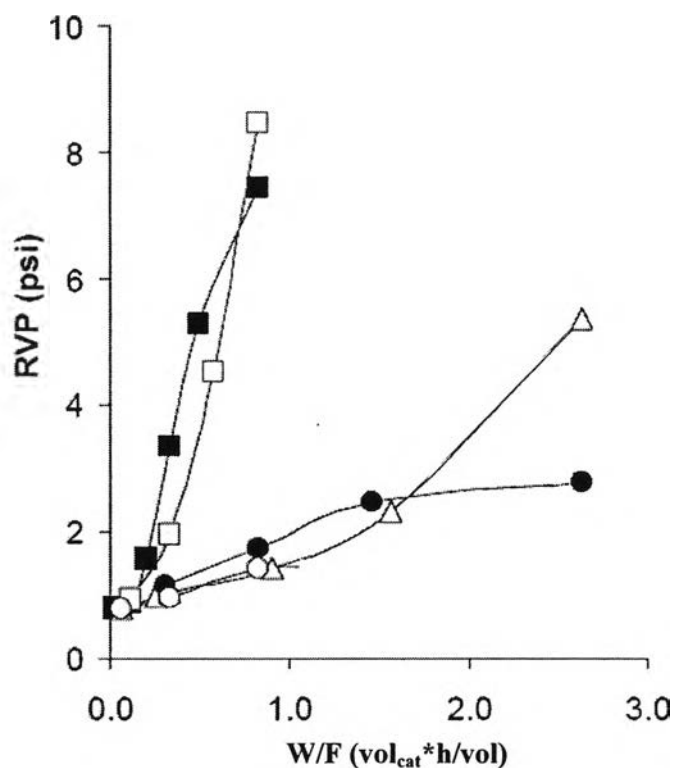
Figure 6.9 Reid vapor pressure (RVP) of product mixture from ring opening of 1,3-DMCH. ■, IrAl; ●, IrSi; △ IrNi0.3Al; □, IrK2.5Al.

A very different trend was obtained on the Ir/SiO_2 and $IrNi_{0.3}/Al_2O_3$ 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 (2MC7 and 4MC7) 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. As mentioned above, the stronger similarity of $IrNi_{0.3}/Al_2O_3$ with Ir/SiO_2 rather than with Ir/Al_2O_3 may be ascribed to the formation of a surface Ni-aluminate that may act as a barrier between Ir and the alumina support.

6.5 Conclusions

The main conclusions drawn from this study can be summarized as follows:

1. The selective ring opening of 1,3-DMCH at unsubstituted C-C bonds, leading to branched products with high octane numbers, is more favored on Ir/SiO_2 than on Ir/Al_2O_3.

2. As the conversion increases, secondary hydrogenolysis of the primary products affects the resulting octane number and increases the vapor pressure of the product. On the Ir/SiO_2 catalyst, branching is preserved due to the preferential cleavage at the unsubstituted C1-C2 terminal bonds. As a result, the yield of products of high octane number is higher on Ir/SiO_2 than on Ir/Al_2O_3.

3. The addition of K to the Ir/Al_2O_3 catalyst results in decreasing secondary hydrogenolysis, but did 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/Al_2O_3 catalyst.

4. The presence of Ni on IrAl at appropriate molar ratios suppresses the cleavage of C-C bonds at substituted positions, thus making the alumina-supported catalyst behave more like a silica-supported catalyst, giving the products with improved octane number and moderate vapor pressure.

6.6 Acknowledgments

6.7 References

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