

Influence of Support Material on the Activity and Selectivity of Pt–Ir Catalysts for Ring Opening Reactions

María Ana Vicerich · Viviana Mónica Benitez ·
María Amparo Sánchez · Carlos Luis Pieck

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Abstract The influence of the supports (Al_2O_3 , TiO_2 and SiO_2) on the activity and selectivity of Pt–Ir catalysts for the ring opening (RO) of decalin was studied. It was found that the properties of the supports strongly influence the distribution, size and Pt–Ir interaction of the metal particles. They therefore also influence the catalytic activity for reactions like dehydrogenation and hydrogenolysis, but also specifically the activity for RO reactions of naphthenes. Via their acid sites the supports influence RO reactions although the effect is not very marked on conversion because the acidity differences are not very significant among them. The results show that the highest decalin conversion for three different supports, alumina, silica and titania, is obtained with the catalysts of highest metal loading. The best selectivity to RO products is obtained with Pt–Ir(1.0)/ Al_2O_3 catalyst. Moreover this catalyst shows the highest performance for MCP RO.

Keywords Pt–Ir · Bifunctional catalysts · Ring opening · Decalin

1 Introduction

In order to respond to increasingly stringent regulations on environmental protection, it is necessary to produce cleaner fuels. For example, aromatic compounds should be reduced and substituted by branched paraffins in the case of

gasoline, or by linear paraffins in the case of diesel. The process of diesel production is very complex and involves selecting and mixing different fractions of oil to meet technical specifications [1]. Given the constant increase in its consumption, it has been proposed to obtain diesel fuel from light cycle oil (LCO), a residual stream issue by FCC refinery units. This implies a full hydrogenation of aromatic compounds and the subsequent selective RO of the naphthenic compounds to paraffin while avoiding side reactions, particularly hydrogenolysis, which can lead to lighter hydrocarbons.

It is necessary to develop bifunctional catalysts with a suitable balance between acid and metal functions in order to produce the selective ring opening (RO) of naphthenes. The metal sites would be responsible for producing the C–C bond cleavage, while the acid function is needed to produce the preliminary ring contraction (RC) from 6 to 5 carbons, the latter being easier to open. However, very strong acid sites can lead to excessive cracking [2–10]. The activity and selectivity of the RO in bifunctional catalysts is strongly dependent on the properties of the metal and the support as well as on the reaction conditions. These parameters include the type and particle size of the metal, the acidity and pore size of the support, and the balance between the metal and acid sites. The working conditions, e.g. temperature, hydrogen pressure, should also be considered.

Decalin is the total product of the hydrogenation of naphthalene and is frequently used as a model molecule to study the SRO. Kubicka et al. [4] and Santikunaporn et al. [2] reported that decalin suffers first RC into the acid function of the catalyst and then the opening is promoted by a metal function. It has also been reported that the addition of Pt to an acidic support reduces the amount of Brønsted acid sites and significantly improves the opening

M. A. Vicerich · V. M. Benitez · M. A. Sánchez ·
C. L. Pieck (✉)
Instituto de Investigaciones en Catálisis y Petroquímica
(INCAPE) (FIQ-UNL, CONICET), Santiago del Estero 2654,
S3000AOJ Santa Fe, Argentina
e-mail: pieck@fiq.unl.edu.ar

and isomerization of decalin [4]. The experimental results indicate that the most active catalysts are the Ir supported ones. These catalysts produce a smaller breakdown of the exocyclic chain though the more beneficial distribution of products is achieved on five-ring carbon atoms and not on six-ring atoms. One solution is to promote RC using a support with medium acid strength.

The supports play an important role in heterogeneous catalysis. In many catalytic processes these are not inert and modify the catalytic properties of the metal particles through electronic interactions or by steric hindrance that ultimately affect the adsorption of the reagents [3]. The supports serve as the network on which the active species are deposited. The supports in general have no catalytic properties of their own; however they can strongly influence the reactions and modify the selectivity and activity of the catalysts.

This work analyzes the influence of different supports (Al_2O_3 , TiO_2 and SiO_2) on the catalytic activity and selectivity of Pt–Ir catalysts for the selective opening of decalin and methylcyclopentane. In addition a comparative study of the properties of different supported catalysts is presented.

1.1 Experimental

1.1.1 Catalyst Preparation Methods

$\gamma\text{-Al}_2\text{O}_3$ (Cyanamid Ketjen CK-300, pore volume = $0.5 \text{ cm}^3 \text{ g}^{-1}$, $S_g = 180 \text{ m}^2 \text{ g}^{-1}$, 35–80 mesh) was calcined during 4 h at 500 °C under flowing dry air. TiO_2 (pore volume = $0.8 \text{ cm}^3 \text{ g}^{-1}$, $S_g = 80 \text{ m}^2 \text{ g}^{-1}$, 35–80 mesh) was calcined during 2 h at 500 °C under flowing dry air. The X-ray diffraction of prepared TiO_2 mainly shows an anatase structure with some traces of rutile phase. SiO_2 (Hi-Sil 210; pore volume = $2.4 \text{ cm}^3 \text{ g}^{-1}$, pH 6.5–7.5) was calcined during 4 h at 500 °C. The samples were left in contact for 1 h at room temperature with the amount of aqueous solutions of metallic precursors (H_2PtCl_6 and H_2IrCl_6) required for producing the desired metal loading. The resulting catalyst slurry was kept at 70 °C and the solvent was evaporated until a dry solid was obtained. The drying process was completed in an oven (at 120 °C overnight) and the samples were then stabilized by calcination under flowing air (4 h at 500 °C) and finally reduced in hydrogen (450 °C for 4 h). All heating steps were performed at $10 \text{ }^\circ\text{C min}^{-1}$. The concentration of aqueous solutions of metallic precursors salts was adjusted to obtain the following metal weight loadings on the finished catalysts: 1.0 %Pt–0.3 %Ir, 1.0 %Pt–1.0 %Ir, 1.0 %Pt–2.0 %Ir, 1.0 %Pt and 0.3 %Ir. Hereafter the catalysts are labeled Pt–Ir(x)/ Al_2O_3 , Pt–Ir(x)/ TiO_2 or Pt–Ir(x)/ SiO_2 where x denotes the content (wt%) of Ir.

1.1.2 Evaluation of the Pt and Ir Contents

The composition of the metallic phase was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution and dilution.

1.1.3 Specific Surface Area

The specific surface area (BET method), total pore volume, and pore size distribution (BJH method) were determined by nitrogen adsorption. The catalyst samples were degassed at 200 °C for 2 h, and then the nitrogen adsorption isotherm was determined at 77 K. A Micromeritics 2100E instrument was used for the experimental measurements.

1.1.4 Temperature-Programmed Reduction (TPR)

This technique allows gathering information about the interaction of the metal components by means of the measurement of the hydrogen consumption during the reduction of surface oxide species at constant heating rates. The temperature at which reduction occurs and the number of reduction peaks depends on the oxidation state of the metals, the interaction of the oxides among them and with the support, and the possible catalytic action of one metal or others elements present or generated during reduction. These tests were performed in an Ohkura TP2002 equipment provided with a thermal conductivity detector. Prior to each TPR test, the catalyst samples were pretreated in situ by heating under flowing air at 350 °C during 1 h. Then, they were heated from room temperature to 700 °C at $10 \text{ }^\circ\text{C min}^{-1}$ under a controlled flow gas stream of 5.0 % hydrogen in argon.

1.1.5 Temperature-Programmed Desorption of Pyridine (TPD)

The amount and strength distribution of acid sites were assessed by means of the temperature-programmed desorption of pyridine (Py). 200 mg of catalyst were first immersed for 4 h in a closed vial containing pure pyridine (Merck, 99.9 %). Then the vial was opened and the excess base was allowed to evaporate at room conditions until apparent dryness. The sample was then loaded into a quartz tube of 0.4 cm diameter over a quartz wool plug. A constant flow of nitrogen ($40 \text{ cm}^3 \text{ min}^{-1}$) was kept through the sample. A first step of desorption of weakly physisorbed base and sample stabilization was performed by heating the sample at 110 °C for 1 h. Then the temperature of the oven was raised to a final value of 600 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The reactor outlet was directly connected to a gas chromatograph equipped with a flame ionization detector.

1.1.6 Isomerization of 3,3-Dimethyl-1-butene (33DMBI)

This reaction was used to selectively and quantitatively determine the concentration of the Brønsted sites of the catalyst. The conditions of the reaction are detailed in [11].

1.1.7 Dynamic Chemisorption of CO

This technique was used to estimate the metal particles on the surface of the catalyst. Calibrated pulses of the adsorbate were injected to a stream of inert gas that flowed over the sample. These pulses were sent to the reactor until the sample was saturated. At the beginning of the experiment, the sample (150 mg) was reduced at 400 °C (10 °C min⁻¹) for 1 h. Then, nitrogen was flown over the sample for 1 h at 500 °C in order to eliminate adsorbed hydrogen. Finally, the sample was cooled down to room temperature under nitrogen flow and 0.6 μmol of CO were sent to the reactor. Non-chemisorbed CO was quantitatively transformed into CH₄ over a Ni/Kieselguhr catalyst and detected in a flame ionization detector connected on-line. The error of the method was estimated by means of nine chemisorption tests of a Pt/Al₂O₃ catalyst with a dispersion of 40 %. The average deviation was found to be 4.3 %.

1.1.8 Cyclopentane (CP) Hydrogenolysis

The reaction was performed in a glass reactor (length 60 cm, diameter 1 cm) under the following conditions: catalyst mass 150 mg, temperature: 300 °C, pressure 0.1 MPa, H₂ flow rate 40 cm³ min⁻¹, cyclopentane flow rate 0.483 cm³ h⁻¹. The reaction equipment has a preheater in order to evaporate the liquid feed and heat the hydrogen to 250 °C. Cyclopentane was fed to the reactor using a syringe pump. Before the reaction was started, the catalysts were conditioned under flowing H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed by online gas chromatography using a ZB-1 capillary column. Values of initial conversion at 10 min time-on-stream are reported.

1.1.9 Cyclohexane (CH) Dehydrogenation

The reaction was performed in a glass reactor (length 60 cm, diameter 1 cm) under the following conditions: catalyst mass 50 mg, temperature: 300 °C, pressure 0.1 MPa, H₂ flow rate 36 cm³ min⁻¹, cyclohexane (CH) flow rate 0.727 cm³ h⁻¹. The reaction equipment has a preheater in order to evaporate the liquid feed and heat the hydrogen to 250 °C. The CH was introduced into the reactor using a syringe pump. Before the reaction was started, the catalysts were reduced with H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed by

online gas chromatography using a ZB-1 capillary column. All points reported are mean values obtained by averaging 12 consecutive measurements equally spaced along the run time. No significant catalyst deactivation was observed in any run.

1.1.10 Methylcyclopentane (MCP) Ring Opening (RO)

The reaction was performed in a glass reactor (length 60 cm, diameter 1 cm) at atmospheric pressure. Before the reaction, samples were reduced with H₂ at 250 °C for 1 h. The conditions used were: catalyst mass = 135 mg, H₂ flow rate = 36 cm³ min⁻¹, MCP flow = 0.362 cm³ min⁻¹, reaction temperature = 250 °C, reaction time = 2 h. The reaction equipment has a preheater in order to evaporate the liquid feed and heat the hydrogen to 250 °C. The reaction products were analyzed on a Varian CX 3400 gas chromatograph equipped with a capillary column Phenomenex ZB-1 connected online.

1.1.11 Decalin Ring Opening (RO)

All SRO experiments were performed in a stainless steel, autoclave-type stirred reactor. The reaction conditions were: temperature = 300–325–350 °C, hydrogen pressure: 3 MPa, stirring rate = 1,360 rpm, volume of decalin = 25 cm³, catalyst loading = 1 g and reaction time = 6 h. A sample was taken at the end of the experiments and it was analyzed using a Varian 3400 CX gas chromatograph equipped with a capillary column (Phenomenex ZB-5) and FID.

2 Results and Discussion

The chemical analysis determined by ICP-OES of catalysts has shown metal contents in close agreement with the expected theoretical ones for all the samples (results not shown).

Table 1 shows the values of specific surface area, mean radius and pore volume of the three supports studied. Al₂O₃ showed the higher surface area, SiO₂ had the largest pore volume, while TiO₂ had the greatest pore radius. It is important to point out that in all cases, given the low metal

Table 1 Surface area, volume and diameter of pore of the supports

Physical property	SiO ₂	TiO ₂	Al ₂ O ₃
Superficial area	130 m ² /g	59 m ² /g	189 m ² /g
Micropore volume	0.0065 cm ³ /g	0.0000 cm ³ /g	0.0102 cm ³ /g
Pore volume	0.53 cm ³ /g	0.28 cm ³ /g	0.48 cm ³ /g
Mean pore radius	47 Å	80 Å	51 Å

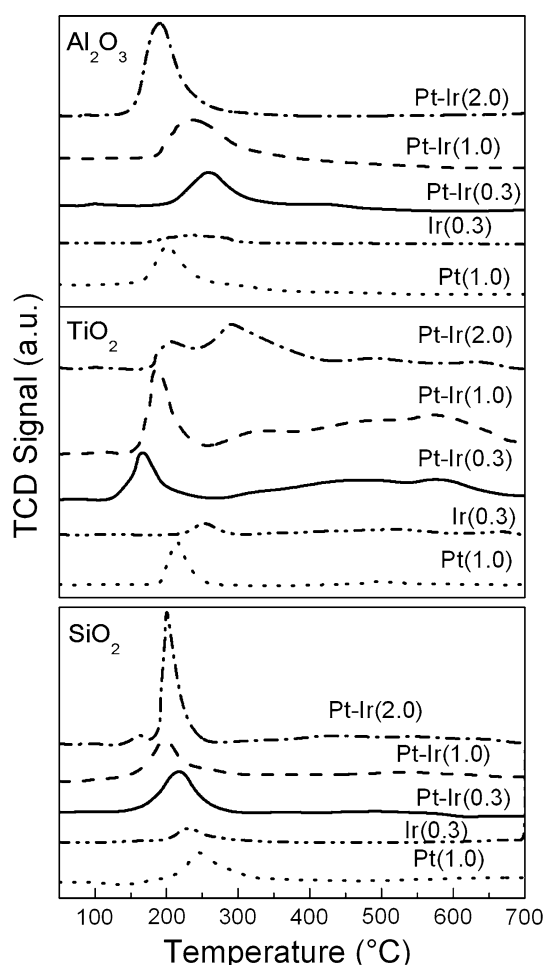


Fig. 1 TPR profiles of Pt–Ir catalysts supported on Al_2O_3 , TiO_2 and SiO_2

charge; the physical properties of the supports did not change by the incorporation of the metals.

Temperature-programmed reduction (TPR) allows to get information about the interaction of the metal components by means of the measurement of the hydrogen consumption during the reduction of the oxides at a constant heating. The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the oxides among them and with the support and on the possible catalytic action of Pt or other elements present or generated during reduction. Figure 1 shows the TPR traces of the different catalysts. In the case of the monometallic catalysts supported on SiO_2 the reduction peak of Ir oxides appeared at a lower temperature than the reduction peak of Pt oxides, while for the TiO_2 and Al_2O_3 supports, the opposite occurred. Carnévilier et al. [12] reported that the low temperature reduction peaks corresponded to large particles, whereas the reduction peaks at higher temperatures were due to the reduction of well-dispersed oxide species. Smaller particles would interact more strongly with the support thus

delaying the reduction. Therefore Pt particles must be more dispersed than Ir on SiO_2 . In the case of bimetallic catalysts, it could be seen that in the three supports the interaction between Pt and Ir was strong since only one reduction peak was observed (except for the Pt–Ir(2.0)/ TiO_2 catalyst). This reduction peaks corresponded to a simultaneous reduction of the two components that form the metal phase. In the case of the Pt–Ir(2.0)/ TiO_2 catalyst two reduction peaks could be seen; a first peak at 205 °C that could be attributed to Pt-rich Pt–Ir ensembles and a second peak at 291 °C that would correspond either to the reduction of Pt–Ir ensembles rich in iridium or to the reduction of segregated iridium species [13]. The experimental results showed that monometallic Pt and Ir catalysts had a reduction peak at different temperatures. The only reduction peak found on the bimetallic catalysts on the three supports clearly indicated a strong interaction between Pt and Ir.

The CO/M (where $M = \text{Pt} + \text{Ir}$) values obtained by CO chemisorption on the supported metals are shown in Table 2. Monometallic Pt/ SiO_2 had the highest value of CO/M according to the smaller particle size estimated by TPR and in agreement with the report of Carnévilier et al. [12]. For the bimetallic catalysts the values of CO/M did not have a definite trend in relation to the support. The Pt–Ir(2.0)/ SiO_2 and Pt–Ir(2.0)/ Al_2O_3 catalysts had the lowest and highest values of CO/M of the bimetallic catalysts, respectively.

The pyridine thermodesorption technique provides valuable information about the support acidity and acid strength distribution. It can be seen in Fig. 2 that the acid sites distribution was similar for the three series of catalysts because they had practically the same desorption temperature. On the bimetallic catalysts the increases of Ir content slightly shifted the desorption peak to higher temperatures. The supported catalysts on Al_2O_3 and SiO_2 had a broad desorption peak attributed to a heterogeneous distribution of the acid strength. TiO_2 series had at least two desorption peaks in the same range of temperature. The area under the desorption trace is proportional to the total acidity. Figure 3 shows that the acidity was slightly increased upon Ir addition in the case of the catalysts supported on Al_2O_3 and

Table 2 CO/M values obtained by CO chemisorption of the Pt–Ir catalysts supported on Al_2O_3 , TiO_2 and SiO_2

Catalysts	Al_2O_3	TiO_2	SiO_2
Pt	54	60	67
Pt–Ir(0.3)	43	49	46
Pt–Ir(1.0)	45	39	42
Pt–Ir(2.0)	56	33	28
Ir	44	21	45

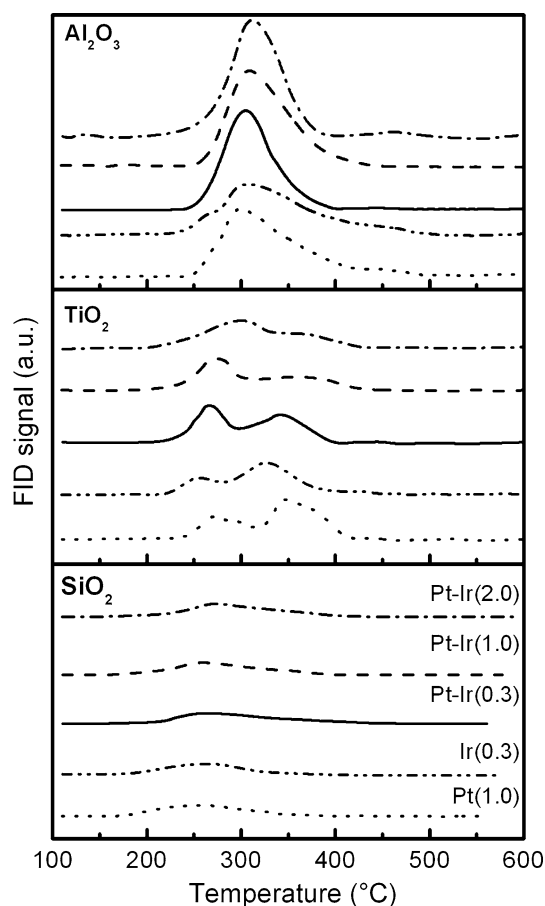


Fig. 2 Pyridine TPD profiles of Pt-Ir catalysts supported on Al_2O_3 , TiO_2 and SiO_2

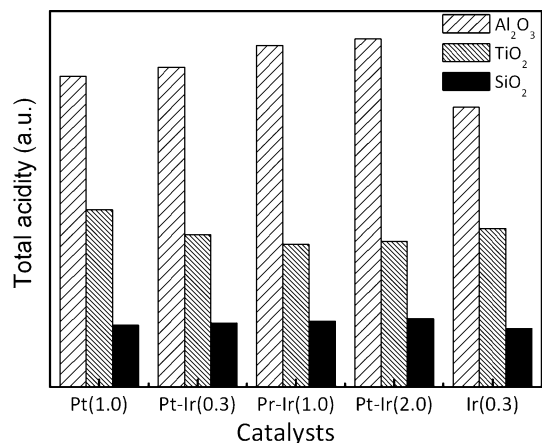


Fig. 3 Acidity obtained by TPD of Pyridine for catalysts supported on Al_2O_3 , TiO_2 and SiO_2

SiO_2 . This trend is easily explained by taking into account that Ir oxides have an acid character. However an opposite behavior was observed in the case of the catalysts supported on TiO_2 . This anomalous phenomenon could be related to migration of TiO_x ($x < 2$) during reduction

treatments of the catalysts. TiO_x species could partially block the acid sites of the metal phase [13, 14]. Moreover, it can be seen that the catalysts supported on Al_2O_3 are more acid than those supported on TiO_2 . The catalysts supported on SiO_2 had the lowest acidity of the three series. For example, the Pt/SiO_2 catalyst has only 20 % of the acidity of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Novaro et al. [11] reported that the acidity of the support decreased in the following order: $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$.

It is known that the skeletal isomerization of 3,3-dimethyl-1-butene (33DM1B) is relatively simple with only two reaction products: 2,3-dimethyl-1-butene (23DM1B) and 2,3-dimethyl-2-butene (23DM2B). At higher reaction temperatures ($>300^\circ\text{C}$) other products appear, mainly methyl pentanes [15]. The slowest step of the reaction is the isomerization of the intermediary carbocation which is produced by methyl migration. The skeletal isomerization of 33DM1B and the migration of the $\text{C}=\text{C}$ double bond occur by the migration of the intermediary carbenium ion on the Brønsted acid sites. Under the reaction conditions used (250°C) only 23DM2B and 23DM1B were obtained, showing that the reaction only proceeded on the Brønsted acid sites. Previous experiments performed on Al_2O_3 supported catalysts showed that reduction and calcination have no influence on the conversion values of 33DM1B. It is important to note that the metal content does not change the conversion value significantly [16]. This means that metallic sites are not involved in the reaction. Brønsted acidity depends almost exclusively on the properties of the support. Therefore the 33DM1B conversion is proportional to the amount of Brønsted acid sites of the support. As expected Fig. 4 shows that Al_2O_3 had a higher Brønsted acidity than the other two supports while SiO_2 scarcely had Brønsted acid sites. These results are in agreement with the total acidity determined by pyridine

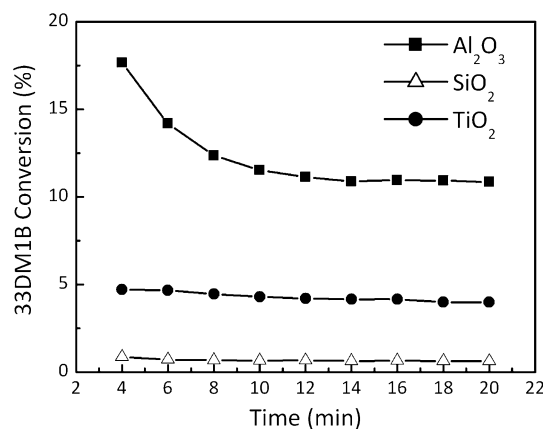


Fig. 4 Conversion obtained by isomerization of 33DM1B for catalysts Pt(1.0) supported on Al_2O_3 , TiO_2 and SiO_2 . (Pretreatment 1 h at 450°C in H_2 , reaction temperature 250°C)

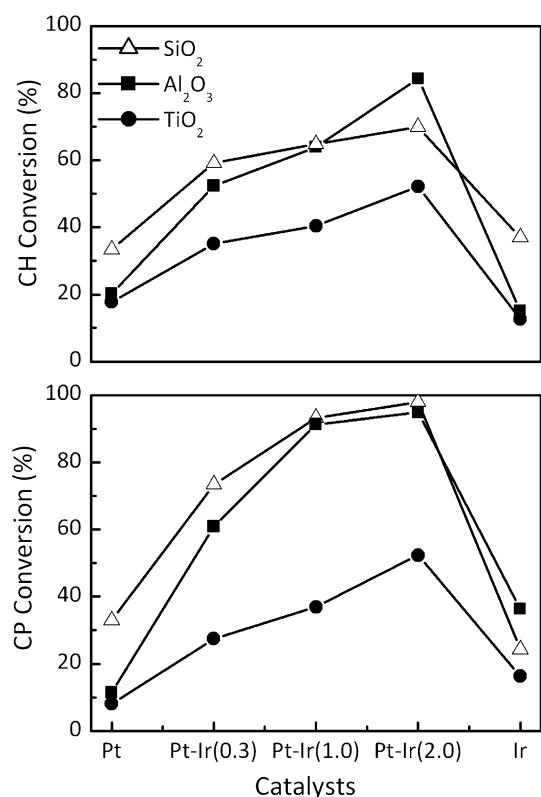


Fig. 5 Conversion obtained on cyclohexane dehydrogenation and cyclopentane hydrogenolysis for catalysts supported on Al_2O_3 , TiO_2 and SiO_2

desorption. The 23DM1B/23DM2B ratio did not change during the reaction, its value being 0.51, 0.42 and 0.60 for Al_2O_3 , TiO_2 and SiO_2 , respectively.

In a previous work [16], we reported that the metal content did not change significantly the conversion value of 33DM1B. Therefore, the Brønsted acidity depended strongly on the support and is affected to a lesser degree by the metal content. In a similar way, the total acidity (Brønsted and Lewis) was more influenced by the support than by the metal charge of the catalysts.

The reaction of CH dehydrogenation to benzene can be used as an indirect method to characterize the metal sites on supports of mild to moderate acidity such as alumina or silica; the reaction rate is proportional to the number of active surface metal atoms. It has the property of being insensitive to the structure of the catalyst, i.e., it does not need a special ensemble of atoms [17]. On the other hand, the hydrogenolysis reaction is known to be a “structure sensitive” or “demanding” reaction; therefore highly dispersed metal crystallites have low activity for such a reaction [18]. Moreover it has been found that Ir has a higher hydrogenolytic activity than Pt [19] and that Pt–Ir bimetallic ensembles are much more active than any of these metals alone [20].

Table 3 Values of cyclopentane conversion/cyclohexane conversion ratio

Catalyst	Al_2O_3	TiO_2	SiO_2
Pt	0.56	0.46	0.99
Pt–Ir(0.3)	1.16	0.78	1.24
Pt–Ir(1.0)	1.43	0.91	1.44
Pt–Ir(2.0)	1.12	1.01	1.40
Ir	2.39	1.28	0.66

Figure 5 shows the conversion values obtained in the CH dehydrogenation and cyclopentane hydrogenolysis reactions. The conversion increased with the metal charge as both metals are active in CH dehydrogenation and cyclopentane hydrogenolysis. It can be seen that the higher conversion values in both reactions were always obtained with the catalysts with the higher metal contents. At equal metal content (except Pt–Ir(2.0)/ SiO_2 catalyst) the series supported on SiO_2 had a higher dehydrogenation activity than the catalysts supported on Al_2O_3 and TiO_2 . This could be due to the fact that platinum and iridium were more dispersed on SiO_2 (except Pt–Ir(2.0)/ SiO_2 catalyst which had low dispersion and low dehydrogenation activity). The lower activity of the catalysts supported on TiO_2 could be due to the migration of TiO_x species during the reduction step of the catalysts [21] which could produce a partial blockage of Pt and Ir species [22–25]. Poondi and Vannice [14] proposed that active sites at the Pt– TiO_2 interface are created while simultaneously the ensembles of Pt and Ir required for hydrogenolysis are destroyed. Moreover Tauster et al. [26] found that the chemical properties of noble metals can be drastically affected by the interaction with the surface of TiO_2 .

Table 3 shows the values of the cyclopentane conversion/CH conversion ratio (parameter of demanding/not demanding reaction) of the three series of catalysts. It can be seen that the catalysts supported on SiO_2 had a higher CP/CH ratio than the same catalysts supported on Al_2O_3 and TiO_2 (except Ir/ SiO_2). The lower values of CP/CH were obtained with the catalyst supported on TiO_2 . These trends are easily explained considering the migration of TiO_x species mentioned above that decrease strongly the hydrogenolysis activity and much less the activity in the CH reaction. This is due to the demanding or no demanding character of the reactions. The higher CP/CH ratio of the catalysts supported on SiO_2 could be due to the lower acidity of the SiO_2 which favors the migration of Pt and Ir leading to the creation of Pt–Ir (as it was found by TPR) ensembles. As mentioned above, Pt–Ir bimetallic ensembles were much more active than any of these metals alone. The results had also shown that the catalysts with Pt/Ir = 1 ratio produce a higher CP/CH ratio.

Table 4 Conversion, selectivity to ring opening products (RO) and n-C₆/3MP and 2MP/3MP molar ratio at 15 min time-on-stream for the SRO of MCP on the catalysts supported on Al₂O₃, TiO₂ and SiO₂

Catalysts	Conversion (%)	Selectivity to RO (%)	Molar ratio	
			n-C ₆ /3MP	2MP/3MP
Pt(1.0)/Al ₂ O ₃	5.6	72	2.9	1.3
Pt-Ir(0.3)/Al ₂ O ₃	12.3	65	1.3	1.2
Pt-Ir(1.0)/Al ₂ O ₃	28.7	71	0.7	1.7
Pt-Ir(2.0)/Al ₂ O ₃	41.9	65	0.8	1.5
Ir(0.3)/Al ₂ O ₃	4.8	67	39.8	2.1
Pt(1.0)/TiO ₂	3.2	64	6.3	2.5
Pt-Ir(0.3)/TiO ₂	26.1	86	0.5	1.9
Pt-Ir(1.0)/TiO ₂	44.4	95	0.1	2.6
Pt-Ir(2.0)/TiO ₂	71.5	90	0.2	1.8
Ir(0.3)/TiO ₂	5.9	75	–	–
Pt(1.0)/SiO ₂	12.1	70	1.9	0.7
Pt-Ir(0.3)/SiO ₂	58.2	86	0.9	2.5
Pt-Ir(1.0)/SiO ₂	70.8	65	0.5	2.1
Pt-Ir(2.0)/SiO ₂	98.0	4	0.4	1.8
Ir(0.3)/SiO ₂	28.8	54	0.9	1.4

The RO reaction of methylcyclopentane (MCP) (monocyclic naphthene) has been widely used as a test reaction [27]. Differences in the product distribution in the MCP RO are attributed to the intrinsic nature of the metals, the metal dispersion, the nature of the support, the hydrocarbon adsorption mode and the experimental conditions [27]. Galperin et al. [28] report two mechanisms for RO of MCP: the selective mechanism which produces 2MP and 3MP in large metal particles and the non-selective mechanism which produces 2MP, 3MP and nC₆ in small metal particles. 2MP and 3MP are produced exclusively on the metal sites, while formation of CH, benzene and n-hexane requires both sites, i.e. acid and metal sites.

Table 4 shows the values of conversion and selectivity obtained at 15 min time-on-stream of the MCP RO reaction for the different catalysts. It could be seen that increasing the load of iridium the conversion in all cases increased. The Pt-Ir(2.0) catalyst was always the most active catalyst of the series regardless of the support. Moreover for the same metal charge the most active catalysts were those supported on SiO₂, followed by the titania supported ones. The least active were those supported on Al₂O₃. It is important to point out that the Pt-Ir(2.0)/SiO₂ catalyst had the highest conversion, resulting in a very low selectivity to RO products. Therefore, the most adequate catalyst to produce RO products was Pt-Ir(2.0)/TiO₂ due to its high selectivity to RO products.

Maire et al. [29] concluded that the product distribution in RO reactions depends on the operating reaction mechanisms. According to a non-selective reaction path that would occur on small metallic particles, with the same breaking probability for any of the cyclic bonds, a product ratio

nC₆:2MP:3MP of 2:2:1 is expected. On the other hand if a selective mechanism operates where the breaking of substituted endocyclic bonds is forbidden, such product ratio would be 0:2:1. Such mechanism would proceed on metallic aggregates of a bigger size. An alternative mechanism, partially selective, with an intermediate product distribution ratio, could also be possible. According to the values of the nC₆/3MP and 2MP/3MP ratio reported in Table 4 it can be concluded that all the bimetallic catalysts exhibit an intermediate behavior between selective and non-selective mechanism because the values of the nC₆/3MP ratio were between 0 and 2. However, the selective mechanism becomes more important when the load of iridium increases, thus decreasing the molar nC₆/3MP ratio.

The decalin reaction products were classified considering the criterion used by Santikunaporn et al. [2] and Chandra Mouli et al. [30, 31] where the reaction products are lumped according to: (i) Cracking products (C₁–C₉ products): 2-methyl butane, hexane, 2,3-dimethyl pentane, 3-methyl-pentane, 5-methyl, 1-hexene, methylcyclopentane, propyl-cyclopentane, 2-methyl-propylcyclopentane, 1,1-dimethyl-cyclopentane, CH, methylcyclohexane, propylcyclohexane, cis 1-ethyl-2-methylcyclohexane, trans 1-ethyl-4-methyl-cyclo-hexane, 1-ethyl-3-methylcyclohexane, 1,1,4-trimethyl-cyclohexane; (ii) Ring opening (RO) C₁₀ products: alkyl-cyclohexanes, alkylcyclopentanes cyclohexenes or benzene (for example: 1-methyl-2-propylcyclohexane, diethylcyclohexane, cis and trans 1,1,3,5-tetramethylcyclohexane, 2-methylpropyl-1-benzene), alkylheptanes, alkylhexanes, alkylpentanes; (iii) RC products: 2,2,3-trimethyl bicycle [2.2.1] heptane, 2,6,6-trimethyl bicyclo[3.1.1]heptane, 1,1-bicyclopentyl, spiro[4.5]-decane, 3,7,7-trimethyl bicyclo[4.1.0]heptane; (iv) Other products: 1-methylindan, cis and trans decahydronaphthalene,

1,2-dihydronaphthalene, 1,2,3,4-tetrahydronaphthalene and including other heavy dehydrogenation products.

Decalin RO was performed at three temperatures (300, 325 and 350 °C) for all the three series of catalysts. As it is expected the conversion increases with temperature since the reaction has a relatively high activation energy. Therefore, an increase of the reaction temperature increases the reaction rate. The selectivity to dehydrogenated products also increases with the reaction temperature. This reaction is reversible and endothermic and produces naphthalene among other dehydrogenated products. Due to its endothermicity the equilibrium conversion to naphthalene is higher at higher temperatures [18]. On the other hand, the selectivity to cracking products, in general, also increases with the reaction temperature because it has the highest activation energy [18]. The RC reaction is catalyzed by the acid sites of the catalyst. It should form rings of five carbon atoms that due to the tension of the C–C bonds would be easier to break forming the desired products. These are intermediate products; therefore, the more active catalysts would produce low amounts of them. Their evolution with the reaction temperature is complex since on the one hand an increase of the reaction temperature promotes their formation, and on the other hand these intermediates are transformed into other compounds. For the sake of simplicity only the results obtained at 325 °C where the selectivity to RO products was maximum are reported.

Table 5 shows the conversion and selectivity obtained in the RO reaction of decalin at 325 °C with catalysts

Table 5 Conversion and selectivity to RO products values obtained in the decalin reaction on Pt–Ir(x) catalysts supported on Al₂O₃, TiO₂ and SiO₂ at 325 °C

Catalysts	Conversion (%)	Selectivity (%)			
		RO	CR	RC	DH
Pt(1.0)/Al ₂ O ₃	4.3	12.1	9.0	7.6	71.3
Pt–Ir(0.3)/Al ₂ O ₃	4.4	60.0	7.2	16.4	16.4
Pt–Ir(1.0)/Al ₂ O ₃	9.5	65.9	2.9	6.9	24.3
Pt–Ir(2.0)/Al ₂ O ₃	10.1	40.8	4.7	35.5	19.0
Ir(0.3)/Al ₂ O ₃	7.2	23.5	1.7	8.2	66.6
Pt(1.0)/TiO ₂	4.9	9.7	5.0	15.1	70.2
Pt–Ir(0.3)/TiO ₂	4.1	34.0	10.2	17.4	38.4
Pt–Ir(1.0)/TiO ₂	5.8	46.1	13.9	15.9	24.1
Pt–Ir(2.0)/TiO ₂	9.1	29.6	18.9	34.8	16.7
Ir(0.3)/TiO ₂	6.7	4.7	7.0	7.9	80.4
Pt(1.0)/SiO ₂	5.5	–	–	–	100.0
Pt–Ir(0.3)/SiO ₂	6.1	33.0	8.1	12.1	46.8
Pt–Ir(1.0)/SiO ₂	7.7	37.0	17.2	11.5	34.3
Pt–Ir(2.0)/SiO ₂	9.9	27.0	10.6	11.4	51.0
Ir(0.3)/SiO ₂	5.9	–	–	1.4	98.6

supported on Al₂O₃, TiO₂ and SiO₂. For the three supports the conversion increased as the metal load increased. The difference in acidity of the three series was not enough to produce big differences in the total activity of each series. However, the alumina supported catalysts were more active than the TiO₂ supported ones, possibly due to the aforementioned partial metal blocking by TiO_x ($x < 2$) species. The combined effect of higher metal activity and higher acid amount in the case of the alumina supported catalysts led to a higher activity for decalin RO in comparison with the titania supported catalysts. In the case of the SiO₂ supported series with the lower total and Brønsted acidity, the monometallic Pt/SiO₂ catalyst showed a higher activity than the other two monometallic Pt supported catalysts. Nevertheless, they only produce dehydrogenated compounds. These could be attributed to the higher CO/Pt value of the Pt/SiO₂ catalyst reported in Table 2. The other catalysts of the SiO₂ supported series had a similar activity than the other catalysts with equal metal charge.

The selectivity to the desired RO products was strongly affected by the support. Moreover it was influenced by the metal charge, the bimetallic catalysts being more selective than the monometallic ones. Table 5 shows a maximum to RO selectivity for the catalysts with Pt/Ir = 1, and the catalyst supported on Al₂O₃ was the most selective one. These results are in agreement with the maximum CP/CH ratio shown in Table 3 and showed the importance of the hydrogenolytic activity of the catalysts on the RO products formation. Also the acid function is necessary because the Pt–Ir(1.0) catalysts supported on SiO₂ and Al₂O₃ have the same CP/CH ratio (Table 3) but very different selectivity to RO. Mc Vicker et al. [32] reported that the addition of a ring-contraction acidity function converts alkylcyclohexanes into more easily ring opened alkylcyclopentanes, greatly facilitating selective RO. They also establish that the metal/acid balance is a controllable catalyst property which allows maximization of ring-opening rates and product selectivities and minimization of undesired hydrocracking and secondary acyclic paraffin isomerization reactions. The results reported in Table 5 clearly show that the selectivity to RO products were higher on the bimetallic catalysts supported on Al₂O₃ which had the highest total acidity and Brønsted acidity.

The selectivity to dehydrogenated products was higher for the monometallic catalysts than for the bimetallic catalysts of each series. For an equal metal load the catalysts supported on SiO₂ showed a higher selectivity to dehydrogenated products than the catalysts supported on TiO₂ and Al₂O₃. This means that it is necessary to have metal ensembles with higher hydrogenolytic activity in order to avoid the formation of dehydrogenated products. However if bimetallic and monometallic catalysts are compared it can be seen that the high hydrogenolytic activity of Pt–Ir

ensembles leads to a higher selectivity to cracking products.

3 Conclusions

The properties of the supports strongly influence the distribution, size, and interaction of the components of the metal particles and consequently the catalytic activity of the involved metal-catalyzed reactions: dehydrogenation, hydrogenolysis and naphthenes RO. Via their acid sites the supports influence opening reactions although the effect is not very marked on conversion because their differences in acidity are not very large. The results have shown that the highest decalin conversion was obtained on the more acid support and with the high metal charge. While the best selectivity to RO is obtained with the Pt–Ir(1.0) catalyst which has the higher CP/CH ratio. The MCP RO reaction was more influenced by the metal function. The supported catalysts on SiO₂ had the lowest acidity being the more activated on the reaction of MCP. But the higher selectivity to RO was obtained on the catalysts with medium total acidity.

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