



Selective ring opening of decalin with Pt–Ir/Al₂O₃ catalyst prepared by catalytic reduction

Silvana A. D'Ippolito^a, Viviana M. Benitez^a, Patricio Reyes^b, María C. Rangel^c, Carlos L. Pieck^{a,*}

^a Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

^b Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 3-C, Concepción, Chile

^c GECCAT, Instituto de Química, Universidade Federal da Bahia, Rua Barão de Geremoabo, s/n, Campus Universitário de Ondina, Federação, 40170-290 Salvador, Bahia, Brazil

ARTICLE INFO

Article history:

Received 23 November 2010

Received in revised form 24 January 2011

Accepted 26 January 2011

Available online 20 February 2011

Keywords:

Selective ring opening

Decalin

Catalytic reduction method

Pt–Ir/Al₂O₃

ABSTRACT

The reaction of selective ring opening using alumina supported Pt–Ir catalysts with and without Mg addition was studied. The catalysts were prepared by the method of catalytic reduction, having 1 wt% of Pt whereas the Ir content varied in the range 0.1–0.6 wt%. Electron diffraction showed that the method of preparation leads to catalysts with strong interaction between Pt and Ir being observed the presence of a solid phase of Pt–Ir. In the catalysts without Mg no changes in the hydrogenolysis activity was observed as the Ir content increases. However, a decrease both in acidity and dehydrogenating activity was observed. In the Mg containing catalysts, the addition of Ir increases the acidity, the dehydrogenating and hydrogenolytic activity. For the isomerization reaction of n-pentane it was found that the addition of Ir improves the stability of the catalysts and formation of isomers of C₅ in both series of catalysts (with and without Mg). The conversion of decalin by ring opening depends on the content of Ir for both studied series.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Public and official concern about new energy sources and its environmental impact has steadily increasing in the last decade. Energy providers are continuously seeking for more efficient and clean technologies, with reduced emission of contaminants. According to the European Automobile Manufacturers Association (ACEA) in 2005, sales of diesel cars reached 49.3% in Europe, compared to 14.6% in 1991 due to a lower price of the diesel [1]. Petroleum refining industry needs more capacity to cope with an increasing demand of high quality fuels, with low aromatic, sulfur and nitrogen content and higher cetane number. In the last years both refiners and research groups have devoted considerable efforts to develop suitable catalytic formulations for selective ring opening of cyclic compounds present in heavy fuels. The lowering of S and aromatic content in fuels have been traditionally achieved using well known hydrotreating and hydrocracking technologies [2]. A reduced particulate emission is achieved through these dearomatization process and also cetane numbers increase significantly. Cetane index (CI) is an important parameter which defines the quality of fuel combustion in motors so high values of CI results in a lower NO_x and particulate emissions [3]. The increase

in CI achieved by the hydrogenation of aromatics is not enough due to the relatively low cetane value of the naphthenic produced. This limitation is particularly important for the improvement of high aromatic fractions such as LCO (Light Cycle Oil) from FCC. Ring opening of at least one naphthenic ring is required to achieve the required cetane levels.

Two main reaction types occur during the catalytic ring opening process. A first possible reaction type is the rupture of C–C bonds attached to naphthenic rings, associated with a decreasing in mean molecular weight of products. On the other hand, the main desired reaction (selective ring opening, SRO), does not significantly affect the resulting molecular weight due to the internal nature of C–C ring bonds. Cyclohexane and methylcyclopentane catalytic ring opening have been used as suitable test reactions in many research works [4]. At least two plausible reaction paths have been proposed: a dicarbene-based mechanism, with molecules perpendicularly adsorbed onto the metal surface, and a multiplet mechanism, with horizontally adsorbed species. In the first case, on highly dispersed Pt a statistical distribution of products is obtained, while in the latter the selective cracking of C–C bonds between two secondary carbon atoms is achieved by Ir, Rh or others. Onyestyák et al. [5] and McVicker et al. [6] have studied the ring opening of naphthenes alkyl substituted of C₆–C₁₀. They have demonstrated the catalytic selectivity of Ir for ring opening of cyclopentane. RO rates on Ir are reduced significantly as the degree of alkyl substitution increases, being directly proportional

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: pieck@fiq.unl.edu.ar (C.L. Pieck).

to the number of secondary C–C bonds. As opposed to Ir, Pt is more active to break substituted C–C bonds. However, this activity depends on the *cis/trans* ratio of methyl substituted cyclopentane and decreases with increasing concentration of *trans* isomers. For acid catalysts, as opposed to metal assisted RO, it is believed that the opening of naphthenic rings of C₆ and C₇ proceeds on Brønsted acid sites, being initiated by protolytic cracking and followed by chain reactions involving carbenium ions [7–9].

The mechanism of cracking and isomerization of alkanes on acid catalysts have been widely studied [10–14], and it may also apply to naphthenes with unsaturated C–C bonds. Results from experimental works and predictions of theoretical calculations allow inferring that either protolytic cracking, protolytic dehydrogenation, hydride transfer, skeletal isomerization, and the β -cleavage and alkylation of adsorbed ions [15,16] are involved. The ring opening of more complex molecules with two fused rings has been much less studied. Decalin ring opening reaction can proceed by acid or metal mechanisms as reported in detail by Resasco et al. [17]. Experimental results indicate that more active and suitable catalysts are those based on supported Ir. They lead to a lower occurrence of exocyclic chain breaks, although a favorable product distribution is achieved for rings of 5 carbon atoms and not for 6 atoms rings. One solution is to promote the ring contraction by using a support with medium acidity strength. There are catalysts that perform the conversion of cyclohexane to methylcyclopentane with high selectivity and low deactivation [18]. These catalysts could be coupled with a ring opening catalyst. Acid catalysts could however produce chain branching with the subsequent cetane loss. Some SRO patents propose the use of Ir catalysts added to medium acidity mesoporous support, being the acidity controlled by the addition of alkali ions [19]. Recently, it was reported the experimental use of SRO coupled to catalytic assisted sulfur traps (CAST), indicating that the performance of an SRO-CAST process is superior to traditional hydrocracking to upgrade the diesel fuel of refinery [20].

As it was mentioned before, several works on selective ring opening focus their attention on Pt–Ir supported catalysts prepared by common methods. In our case ring-opening Pt–Ir/Al₂O₃ catalysts were prepared by a non-classical catalytic reduction method. This preparation method has been reported to produce a strong interaction between the metals (Pt–Ir) [21–23]. A strong Pt–Ir interaction is known to enhance the reactions of hydrogenolysis [24]. Moreover the modifications of the acid function by Mg addition have not been reported previously in the open literature. The aim of this study was to evaluate the catalytic properties of Mg doped Pt–Ir/Al₂O₃ catalysts prepared by the catalytic reduction method during the selective ring opening of cyclonaphthenes. A special focus is put on the effect of the support acidity on the activity and selectivity.

The aim of this study was to evaluate the catalytic properties of Pt–Ir/Al₂O₃ catalysts prepared by the catalytic reduction method to produce the selective ring opening and to study the effect of support acidity.

2. Experimental

2.1. Catalysts preparation

Pt/Al₂O₃ catalyst. It was prepared using alumina supplied by Ketjen (CK-300, 200 m² g⁻¹, 0.55 cm³ g⁻¹). The support was crushed and sieved in order to keep particles sizes between 0.25 and 0.40 mm and then they were calcined in flowing air at 650 °C for 4 h. The catalyst was prepared by a conventional impregnation method. Firstly an aqueous solution of HCl (0.2 mol L⁻¹) was added to the support and the system was left for 1 h without stirring at room temperature. Then an aqueous solution of H₂PtCl₆ was added. The

slurry was gently stirred for 1 h at room temperature. Then, it was dried by atmospheric evaporation in a thermostated bath at 70 °C until a dry solid was obtained. The drying was completed in a stove at 120 °C overnight. The concentration of the impregnating solutions was adjusted in order to obtain 1.0 wt% Pt in the final catalyst. Then, the catalyst was calcined in a flowing air system at 300 °C for 4 h, and cooled down to room temperature under flowing nitrogen. Finally the catalysts were reduced under flowing hydrogen (60 cm³ min⁻¹) at 500 °C for 4 h. A heating rate of 10 °C min⁻¹ was employed for all heating steps.

Pt–Mg/Al₂O₃ catalyst. In order to modify the acidity, a solution of Mg(NO₃)₂·6H₂O was added to the Pt catalyst. The Pt/Al₂O₃ catalyst calcined at 300 °C for 4 h was impregnated with Mg solution in order to obtain 1.0 wt% of Mg and was left for 1 h without stirring. Then, it was dried in a thermostated bath at 70 °C until a dry solid was obtained. The drying was completed in a stove at 120 °C. Finally, the Pt–Mg/Al₂O₃ catalyst was calcined (air, 60 cm³ min⁻¹, 300 °C, 10 °C min⁻¹, 4 h) and reduced (H₂, 60 cm³ min⁻¹, 500 °C, 10 °C min⁻¹, 4 h).

Preparation of Pt–Ir–Mg/Al₂O₃ and Pt–Ir/Al₂O₃ catalysts. They were prepared by catalytic reduction by making use of the catalytic action of Pt present in the parent catalyst (Pt) using a special all glass apparatus [25]. Monometallic (Pt) or bimetallic (Pt–Mg) parent catalysts were first reduced at 300 °C for 1 h in hydrogen (60 cm³ min⁻¹) and then cooled down to room temperature under hydrogen flow. Then, a degassed H₂IrCl₆ solution with the appropriate concentration was poured in the reactor. After 1 h of contact with the catalyst under constant hydrogen flow (300 cm³ min⁻¹), the solution was drained. Then, the catalyst was dried at 100 °C under hydrogen overnight. Finally, the catalyst was activated by reduction in hydrogen flow at 500 °C for 2 h. The content of Ir solution was varied in order to obtain 0.1, 0.3 and 0.6 wt% of Ir. The catalysts were named Pt–Ir(*x*) and Pt–Mg–Ir(*x*), where *x* is the nominal content of Ir.

2.2. Catalyst characterization

Measurement of the Pt, Ir and Mg contents. The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution and suitable dilution.

Temperature-programmed desorption of pyridine. This test was used for measuring the amount and strength distribution of the acid sites. Samples of 200 mg were impregnated with an excess of pyridine. Once the excess base had been removed, physisorbed pyridine was eliminated by heating the sample in a nitrogen stream at 110 °C for 1 h. Then, the temperature was raised at a rate of 10 °C min⁻¹ to a final value of 500 °C. To measure the amount of desorbed pyridine, the reactor exhaust was directly connected to a flame ionization detector. The detector signal (in mV) was sampled at 1 Hz and recorded in a computer device. The total amount of adsorbed pyridine was determined by comparing the area under the obtained TPD traces with the area from calibrated pyridine pulses (1–2 μ l) injected to the empty reactor.

Temperature-programmed reduction (TPR). These tests were performed in an Ohkura TP2002 equipment with a thermal conductivity detector. At the beginning of each TPR test the catalyst samples were pretreated *in situ* by heating in air at 400 °C for 1 h. Then, they were heated from room temperature to 700 °C at 10 °C min⁻¹ in a gas stream of 5.0% hydrogen in argon and the corresponding TCD signal was recorded.

Transmission electron microscopy. Transmission electron micrographs (TEM) were obtained in a Jeol JEM 1200 EXII microscope. The supported catalysts were ground in an agate mortar and dispersed in ethanol. A diluted drop of each dispersion was placed on a 150 mesh copper grid coated with carbon. The micrographs

Table 1

Percentage of Ir, the average metal particle diameter obtained by TEM and acid concentration determined by pyridine TPD of Pt–Ir(x) and Pt–Mg–Ir(x) catalysts.

Catalysts	Ir (wt%)	dp (nm)	Total acidity ($\mu\text{mol pyridine/g}$)
Pt (1.0)	–	1.8	490
Pt–Ir(0.1)	0.10	2.1	466
Pt–Ir(0.3)	0.24	2.0	431
Pt–Ir(0.6)	0.42	2.0	304
Ir(0.6)	0.58	2.8	230
Pt–Mg	–	4.3	69
Pt–Mg–Ir(0.1)	0.09	4.2	132
Pt–Mg–Ir(0.3)	0.22	2.4	162
Pt–Mg–Ir(0.6)	0.45	2.6	245
Mg–Ir(0.6)	0.61		83

were obtained in both bright and dark fields. The histograms were obtained by measuring the size of about 200–500 particles; the mean particle size was obtained at the maximum of the histograms. The highest error is about 20% for the smallest particles. An Au standard (Merck 99%) was used for calibration.

2.3. Catalytic experiments

Cyclopentane hydrogenolysis. Before the reaction the catalysts were reduced for 1 h at 500 °C in H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$). Then they were cooled under H_2 to the reaction temperature (350 °C). The other conditions were: catalyst mass = 150 mg, pressure = 0.1 MPa, H_2 flow rate = $40 \text{ cm}^3 \text{ min}^{-1}$, cyclopentane flow rate = $0.483 \text{ cm}^3 \text{ h}^{-1}$. The products were analyzed chromatographically in a Varian 3400 CX chromatograph equipped with a capillary column (Phenomenex ZB-1) and a conventional FID.

Cyclohexane dehydrogenation. The reaction was performed in a glass reactor with the following conditions: catalyst mass = 100 mg, temperature = 300 °C, pressure = 0.1 MPa, H_2 = $80 \text{ cm}^3 \text{ min}^{-1}$, cyclohexane = $1.61 \text{ cm}^3 \text{ h}^{-1}$. Prior the reaction the catalysts were treated in H_2 ($80 \text{ cm}^3 \text{ min}^{-1}$, 500 °C, 1 h). The products were analyzed by capillary GC as described before.

n-pentane isomerization. The reaction was carried out for 4 h in a continuous flow glass reactor at atmospheric pressure, 500 °C, WHSV = 4.5 and molar ratio H_2 :n-C₅ = 6. n-C₅ was supplied by Merck (99.9%). The analysis of reactants and products was performed using the same chromatograph and column as above.

SRO of decalin. All SRO experiments were performed in a stainless steel, autoclave-type stirred reactor. The reaction conditions were: temperature: 350 °C, hydrogen pressure: 3 MPa, stirring rate: 1360 rpm, volume of decalin: 25 cm^3 , catalyst loading: 1 g. 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.

3. Results and discussion

Table 1 shows the Ir content of catalysts as determined by ICP-OES. It can be observed that Ir is not quantitatively deposited by the catalytic reduction method. The amount effectively deposited does not depend on Mg content. This result can be explained by considering that when H_2 is present in the solution, only IrCl_6^{2-} species in contact or in the neighborhood of Pt particles are catalytically reduced by chemisorbed hydrogen and that simultaneously part of Ir is merely adsorbed by electrostatic forces on surface groups of the support. The catalytic reduction reaction is a fast reaction [21] and therefore in the first minutes of impregnation Ir would be deposited mainly near the Pt particles. On the other hand, at longer times Ir deposition would increase mainly on the support. The content of Pt and Mg were 0.92 and 0.84 wt%, respectively.

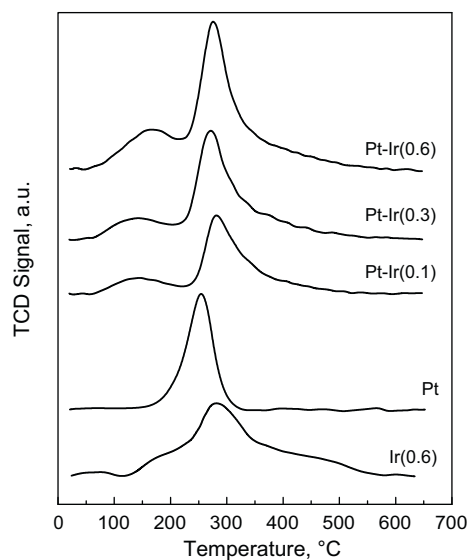


Fig. 1. TPR profiles of Ir and Pt–Ir(x) catalysts.

The amount of pyridine desorbed as a function of temperature gives information about the total amount of acid sites and acid strength distribution. The area under the TPD curve represents the total acidity of the catalysts. Table 1 reports the values of total acidity of the catalysts studied. It can be seen in Table 1 that in the case of Pt–Ir(x) catalysts, the addition of Ir causes a decrease in acidity. The Ir adsorbed species has an acidic character and can replace pre-existing surface Cl groups, leading to lower acid strength sites. The removal of part of the Cl from the support may also occur during the impregnation procedures. For the series of Pt–Mg–Ir(x) catalysts, the trend in acidity with the addition of Ir is opposite to that observed in the catalysts without Mg. It must be pointed out that Mg addition produces a large decrease in the acidity of the support due to its strong basic character. In this case the deposition of Ir could effectively increase the acidity from very low values. In both series of catalysts the TPD profiles (not shown) indicate that the addition of Ir causes a decrease in acid strength (lower desorption temperature). The decrease of acidity is desirable since it allows to lead the hydrogenolytic capacity of metal phase (Pt–Ir) for endocyclic C–C bond cleavage and inhibit the exocyclic breakdown. Moreover, the latter reaction type may be due to the cracking reaction on acid sites of the support. On the other hand, the support acid sites are able to isomerize linear paraffins with a corresponding decrease in cetane number. Therefore, the regulation of the acidity of the support by addition of alkaline promoters (in this case Mg) can improve the selectivity to linear paraffins due to an inhibition of isomerization and cracking. It can be seen in Table 1 that the series of Pt–Ir(x) catalysts the incorporation of Ir does not produce changes in the metal particle size. In the case of Pt–Mg–Ir(x) catalysts a strong decrease in the metal particle size is observed when the content of Ir is higher than 0.3 wt%. Moreover, for catalysts that contain Mg, the metal particles are larger than those found for catalysts without Mg. This is particularly noticeable in samples with low levels of Ir (≤ 0.1 wt%). Electron diffraction (ED) experiments showed that for both series of catalysts a solid solution of Pt and Ir is present. These results are consistent with TPR experiments where a strong interaction between Pt and Ir was observed.

Fig. 1 shows the TPR profiles of the Pt–Ir(x) catalysts and the monometallic Pt and Ir catalysts. It can be seen that the monometallic Ir catalyst has a big peak centered about 285 °C. This peak begins at 100 °C, finishes at 550 °C and has a shoulder at 170 °C. The broad reduction zone witnesses the different interaction between the Ir oxides species and the support and the different particle sizes of

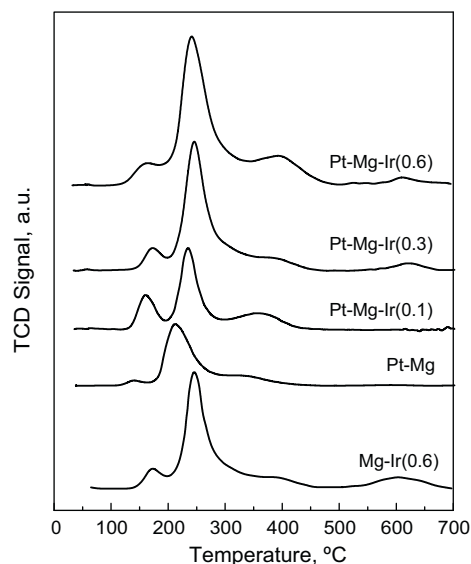


Fig. 2. TPR profiles of Ir–Mg and Pt–Mg–Ir(*x*) catalysts.

the Ir oxide agglomerates. The Pt catalyst has a large reduction peak centered around 254°C. This reduction peak at about 220–260°C has been frequently reported by several authors [26–28]. The TPR traces of the bimetallic Pt–Ir catalysts had two reduction peaks, one at a low temperature (160°C) and one in the 270–280°C range. The peak at 160°C is attributed to the reduction of Pt–Ir ensembles, rich in Pt, while the reduction peak at higher temperatures corresponds to the reduction of Ir-rich ensembles [29]. As the Ir content increases the size of both peaks also increased.

Fig. 2 shows the TPR profiles of the Pt–Mg–Ir(*x*) catalysts and the Ir–Mg catalyst. The Pt–Mg catalyst displays two peaks, one around 140°C and another at 215°C. A shoulder at 350°C can also be seen that can be attributed to the Pt-catalyzed reduction of Mg species. The peaks at 140°C and 215°C correspond to the reduction of Pt [29]. The lower temperature of Pt reduction can be explained by considering that the addition of Mg increases the electron density of Pt [30]. The peak at 140°C can be due to a strong reduction of the Pt-support interaction by Mg addition. Ir–Mg catalysts have four reduction peaks, one at 168°C, another at 245°C, a shoulder at 350°C and a last reduction zone at 600°C. These reduction peaks can be explained in a similar way to the Pt–Mg catalyst. The first peak can be attributed to Ir oxides species in low interaction with the support while the peak at 245°C can be due to Ir oxides species with higher metal-support interaction. The peaks at 350°C and 600°C are due to the reduction of Mg oxides species. The 350°C peak is due to the reduction of Mg oxides catalyzed by Ir. The peak at 600°C could be assigned to a reduction of isolated Mg that was segregated from Ir.

The addition of Ir to Pt–Mg catalysts produces a shift to higher temperatures of the two peaks of reduction of Pt. Moreover an increase of the intensity of the peaks at 160°C and 245°C can be seen as the Ir content is increased. The comparison of the TPR traces of Figs. 1 and 2 shows that the addition of Mg causes a shift of the peak at 270–280°C (Fig. 1) to lower temperatures. This shift could be due to a lower Ir- or Pt-support interaction as a consequence of the lower acidity of the Mg containing supports. In addition, as noted above, the higher electron density of Pt facilitates their reduction [30]. Therefore both Pt and Ir species are reduced at a lower temperature.

Fig. 1 shows the TPR profiles of Pt–Ir(*x*) catalysts. It can be seen that the monometallic Pt catalyst has a large reduction peak centered around 254°C, the bimetallic Pt–Ir catalysts presents two

Table 2

Conversion values obtained in the CP hydrogenolysis, CH dehydrogenation and decalin reaction on Pt–Ir(*x*) and Pt–Mg–Ir(*x*) catalysts.

Catalysts	CP conversion (%)	CH conversion (%)	Decalin conversion (%)
Pt (1.0)	7.4	99.9	7.8
Pt–Ir(0.1)	99.9	92.0	16.1
Pt–Ir(0.3)	98.9	84.0	14.3
Pt–Ir(0.6)	97.3	72.0	12.6
Ir(0.6)	91.4	30.0	6.4
Pt–Mg	8.4	65.0	3.0
Pt–Mg–Ir(0.1)	12.2	70.5	6.2
Pt–Mg–Ir(0.3)	76.6	79.7	11.2
Pt–Mg–Ir(0.6)	89.2	83.0	16.0
Mg–Ir(0.6)	99.0	81.3	22.0

reduction peaks, one at low temperature (160°C) and one in the 270–280°C range. The peak at 160°C is attributed to the reduction of Pt–Ir ensembles, rich in Pt, while the reduction peak at higher temperature corresponds to the Ir-rich ensembles [22]. As the Ir content increases, both reduction peaks are increased.

Fig. 2 shows the TPR profiles of Pt–Mg–Ir(*x*) catalysts. Pt–Mg catalyst displays two peaks, one around 160°C and another at 220°C, both peaks corresponding to the reduction of Pt [22]. The lower reduction temperature of Pt can be explained by considering that the addition of Mg increases its electron density [23]. The presence of a shoulder at 350°C which is assigned to the reduction of Mg species was also observed [23].

The addition of Ir to Pt–Mg catalyst produces a shift to higher temperatures of the three peaks mentioned above. In addition, it can be seen an increase in the intensity of the peak at 160°C and 220°C due to the presence of Ir species. The comparison of the profiles of Figs. 1 and 2 shows that the addition of Mg causes a shift of the peak appearing around 270–280°C (Fig. 1) towards lower temperatures. This shifting could be due to a lower Ir-support interaction as a consequence of the lower support acidity of Mg containing catalysts. In addition, as noted above, the higher electron density of Pt facilitates their reduction [23]. Therefore, both Pt and Ir species are reduced to a lower temperature.

Table 2 shows the values of conversion for cyclohexane (CH) dehydrogenation and cyclopentane (CP) hydrogenolysis as test reactions. The dehydrogenation reaction of CH has 100% selectivity to benzene and suffers no deactivation during the whole experience (1 h), for this reason Table 2 reports the average conversion values (12 points) at the selected operating conditions. On the other hand, the hydrogenolysis reaction produces a series of products, such as n-pentane, propane, ethane, methane, etc. and is rapidly deactivated by coke deposition. Therefore, data are reported at a 5 min time on stream. It is well known that de/hydrogenation reactions can proceed on simple (monoatomic) sites, but hydrogenolysis require catalytic sites of a more complicated morphology (clusters or ensembles) [31–33]. Pioneering works of Boudart and coworkers on structure sensitivity [34] enabled the classification of catalytic reactions as “demanding” (sensitive to morphological structure) or “facile” (structure-insensitive), according to the requirement or not of a particular ensemble of neighboring metal atoms in order to form adsorbate bonds with the proper strength. The dehydrogenation of cyclohexane is a typical metal catalyzed, non-demanding reaction (it does not require the presence of particular atom ensembles) [34] while hydrogenolysis of cyclopentane is a demanding reaction [35], i.e. it needs ensembles of metal atoms with a given configuration. Highly dispersed metal particles have small hydrogenolysis activity [36]. Ir is known to have higher hydrogenolysis activity than Pt and the Pt–Ir ensembles are more active than the individual metals [29]. It can be seen in Table 2 that the conversion of CP is essentially constant and it does not change with the addition of Ir in the Pt–Ir(*x*) catalysts, while the

Table 3

Final values of conversion, selectivity to isoparaffins and methane in the reaction of n-pentane on Pt–Ir(x) and Pt–Mg–Ir(x) catalysts.

Catalyst	X_f (%)	$(X_i - X_f)/X_i$	Sel. i-C ₅ (%)	Sel. C ₁
Pt (1.0)	45.20	0.70	18.20	1.90
Pt–Ir(0.1)	42.40	0.63	6.40	2.60
Pt–Ir(0.3)	32.10	0.51	6.30	4.20
Pt–Ir(0.6)	12.30	0.12	10.90	5.80
Ir(0.6)	11.40	0.48	9.30	6.60
Pt–Mg	12.06	0.39	11.60	3.85
Pt–Mg–Ir(0.1)	14.90	0.25	6.10	3.85
Pt–Mg–Ir(0.3)	29.60	0.13	7.20	3.17
Pt–Mg–Ir(0.6)	33.90	0.09	11.10	2.17
Mg–Ir(0.6)	18.97	0.10	1.12	3.01

X_f : conversion at 240 min; X_i : conversion at 5 min; Sel. i-C₅: selectivity to isomers of C₅; Sel. C₁: selectivity to methane.

Pt–Mg–Ir(x) series with higher content of Ir an enhancement in the hydrogenolysis activity was observed. On the other hand, the addition of Mg causes a decrease in the conversion. These results indicate a strong influence of Mg. Evidently the Mg interacts with the active phase (Pt–Ir), decreasing its activity. Pt–Ir ensembles capable of producing the C–C bond cleavage may be formed at high Ir contents. The catalyst without Mg with lowest Ir loading is very active and a conversion level close to 100% was achieved. It is interesting to analyze the results for CH dehydrogenation. This reaction is a non sensitive one, i.e. it does not need special ensembles of atoms. It may be noted that in the case of Pt–Mg–Ir(x) catalysts the activity for CH dehydrogenation is lower than that found for Pt–Ir(x) catalysts with similar Ir contents with the exception of Pt–Ir(0.6) catalyst. This may be explained considering that Mg is also deposited on metallic sites blocking them for this reaction (Mg itself does not have any activity) and causing the electronic effect mentioned before [30]. Another effect to consider is that due to modification in the metal particle size. According to TEM data (see Table 1) Pt–Ir(x) catalysts have smaller size, i.e., higher metal dispersion than Pt–Mg–Ir(x) catalysts. Therefore, we expect a higher activity in dehydrogenation of the Pt–Ir(x) catalysts. The CH dehydrogenation reaction shows a opposite trend with the addition of Ir in both series. This could be explained by considering that the iridium has lower dehydrogenating capacity than Pt [29]. Therefore, its incorporation results in an activity decrease for the Pt–Ir(x) catalysts series. In the Pt–Mg–Ir(x) series, the activity is lower due to the presence of Mg, and the addition of Ir increases the dehydrogenating capacity of the catalyst.

Table 2 also summarizes the results obtained for decalin conversion measured after 6 h of reaction. Two opposite trends in conversion were noted as Ir is added. The conversion decreases with the addition of iridium in Pt–Ir(x) catalysts, but increases for Pt–Mg–Ir(x) catalysts. The decrease in activity with the addition of Ir observed for Pt–Ir(x) catalysts can be explained considering that hydrogenolysis activity remains almost constant with the addition of Ir while dehydrogenating activity decreases. Conversely, in the case of the Pt–Mg–Ir(x) catalysts the hydrogenolysis and dehydrogenation activity increases with the addition of Ir.

Table 3 displays the conversion values and selectivity to i-C₅ for the reaction of n-C₅. The parameter $(X_i - X_f)/X_i$ represents the decrease in the conversion level from the beginning of the experiment (X_i) to the final conversion (X_f) relative to the initial conversion value. The higher this parameter, the higher the catalyst deactivation. The catalytic transformation of n-pentane on dual function (metal/acid) catalysts yields many products: 1, isopentane, as a consequence of the bifunctional, acid controlled, isomerization reaction; 2, lighter gaseous hydrocarbons (C₂ and C₃) from cracking reactions partly controlled by the metal function and partly by the acidic function; 3, cyclopentane by dehydrocyclyzation on metal sites and 4, methane from hydrogenolysis on the

metallic sites. No aromatic compounds can be formed from nC₅ reforming so the main products are paraffin isomers. It is currently accepted that the C₅ isomerization mechanism is a bifunctional (metal–acid) one [37]. The linear paraffin is firstly dehydrogenated on metal sites, the produced olefin being then isomerized on acid sites. This olefin isomer is finally re-hydrogenated on the metal site and the isoparaffin is obtained. The rate controlling step of this mechanism is the acid catalyzed one [38] so the formation of i-pentane can be taken as a measure of this catalytic function. It has been nevertheless reported that a monofunctional metal-catalyzed mechanism for isomerization may take place through the hydrogenolysis of five carbon atoms rings [36,37], but its contribution at the experimental conditions used here seems to be negligible [39].

It is accepted that the isomerization of n-paraffins occurs by a bifunctional metal–acid mechanism [25]. The reaction starts on the metal sites with the dehydrogenation of the paraffin to an olefin. Then, the linear olefin is converted to a branched one over acid sites and this branched alkene is finally hydrogenated over a metal site. This bifunctional mechanism is controlled by the acid catalyzed step [26], therefore, the yield to isopentane can be taken as an indirect measure of the activity of the acid function.

It can be seen in Table 3 that the Pt–Ir(x) catalysts with increasing Ir content a decrease of the conversion of n-pentane is observed. On the other hand, in Pt–Mg–Ir(x) catalysts series shows that the conversion of n-pentane increases with the Ir content. At similar percentage of Ir, it can be seen that the Pt–Mg–Ir(x) series have a lower conversion of n-pentane than the Pt–Ir series, except the Pt–Mg–Ir(0.6) catalyst. These results are consistent with the acidity values reported in Table 1. The acid function can produce isomers of i-C₅ through the isomerization reaction, gases (C₁–C₃) through the reaction of cracking and coke by polymerization of dehydrogenated precursors produced by the metal function. The acid strength required for cracking reactions is higher than that required for the isomerization reaction. Therefore, the largest i-C₅ selectivity of catalysts with Mg is due to the elimination of strong acid sites. This acidity change promotes the reactions of isomerization at the expense of cracking reactions. For this reason, there is an increases in the selectivity to i-C₅ and a strong decrease of propane selectivity (results not shown) which is a typical product of the cracking reaction. It can be seen in Table 3 that the Pt–Mg–Ir(x) catalysts are more stable than the Pt–Ir(x) catalysts. This is explained taking into account that the formation of coke is a complex reaction where the metal produces the dehydrogenated intermediates and also destroyed them by hydrogenolysis. The acid function is also responsible for the coke formation through the polymerization of dehydrogenated surface intermediates. The lower the acid strength the lower coke deposition and therefore more stable catalysts.

4. Conclusions

It was found that the deposition of Ir on Pt/Al₂O₃ catalyst by the catalytic reduction method produces changes both in the acid and metal functions. The preparation method allows obtaining a strong interaction between Pt and Ir as was confirmed by the presence of a solid phase of Pt–Ir. The activity of the metal function (cyclohexane dehydrogenation and cyclopentane hydrogenolysis) and acidity of the catalysts depend on the contents of Ir and Mg. In the series of catalysts without Mg, the increases of Ir loading produces a decreases in acidity and dehydrogenation activity, while hydrogenolysis activity is almost not affected. When the support contains Mg, the addition of Ir increases the acidity, hydrogenolysis and dehydrogenating capacity. Results for pentane isomerization showed that the addition of Ir promotes stability and the forma-

tion of isomers of C₅ in both series of catalyst (with and without Mg).

Finally, it was found that the conversion of decalin has a different behavior with the addition of Ir. For catalysts prepared without Mg, the conversion decreases upon the addition of Ir, whereas the opposite occurs in the series of catalysts prepared with Mg. The catalysts preparation method used (catalytic reduction) provides catalysts with hydrogenolytic activity that are active in the ring opening of naphthenes.

References

- [1] <http://www.acea.be/images/uploads/pr/20061978att01.pdf>, accessed 2010-10-28.
- [2] T.C. Kaufmann, A. Kaldor, G.F. Stuntz, M.C. Kerby, L.L. Ansell, *Catal. Today* 62 (2000) 77–90.
- [3] B.H. Cooper, B.B.L. Donnis, *Appl. Catal. A* 137 (1996) 203–223.
- [4] F.G. Gault, *Adv. Catal.* 30 (1981) 1–95.
- [5] G. Onyestyák, G. Pál-Borbély, H.K. Beyer, *Appl. Catal. A* 229 (2002) 65–74.
- [6] G.B. McVicker, M. Daage, M.S. Touvelle, C.W. Hudson, D.P. Klein, W.C. Baird Jr., B.R. Cook, J.G. Chen, S. Hantzer, D.E.W. Vaughan, E.S. Ellis, O.C. Feeley, *J. Catal.* 210 (2002) 137–148.
- [7] A. Corma, F. Mocholi, A.V. Orchillés, G.S. Koermer, R.J. Madon, *Appl. Catal.* 67 (1990) 307–324.
- [8] H.S. Cerqueira, P.C. Mihindou-Koumba, P. Magnoux, M. Guisnet, *Ind. Eng. Chem. Res.* 40 (2001) 1032–1041.
- [9] J. Abbot, *J. Catal.* 123 (1990) 383–395.
- [10] J.A. Martens, P.A. Jacobs, *Stud. Surf. Sci. Catal.* 137 (2001) 633–669.
- [11] F.C. Jentoft, B.C. Gates, *Top. Catal.* 4 (1997) 1–13.
- [12] Y. Ono, *Catal. Today* 81 (2003) 3–16.
- [13] A. Corma, P.J. Miguel, A.V. Orchillés, *J. Catal.* 145 (1994) 171–180.
- [14] S.T. Sie, *Ind. Eng. Chem. Res.* 32 (1993) 397–402.
- [15] M.V. Frash, R.A. van Santen, *Top. Catal.* 9 (1999) 191–205.
- [16] A.M. Rigby, G.J. Kramer, R.A. van Santen, *J. Catal.* 170 (1997) 1–10.
- [17] R.C. Santana, P.T. Do, M. Santikunaporn, W.E. Alvarez, J.D. Taylor, E.L. Sughrue, D.E. Resasco, *Fuel* 85 (2006) 643–656.
- [18] W.C. Baird, J.G. Chen, G.B. McVicker, US Patent 6,623,625 (2003).
- [19] K. Shimizu, T. Sunagawa, C.R. Vera, K. Ukegawa, *Appl. Catal. A* 206 (2001) 79–86.
- [20] M. Daage, J. Santiesteban, XIX Simp. Iber. Catal., Mérida, México, 5/09/2004, Plenary Conf.
- [21] C.L. Pieck, P. Marecot, J. Barbier, *Appl. Catal. A* 134 (1996) 319–329.
- [22] C.L. Pieck, C.A. Querini, J.M. Parera, P. Marecot, J. Barbier, *Appl. Catal. A* 133 (1995) 281–292.
- [23] C. Carnevillier, F. Epron, P. Marecot, *Appl. Catal. A* 275 (2004) 25–33.
- [24] V. Pomec, *Adv. Catal.* 32 (1983) 149–214.
- [25] M. Boutzeloit, V.M. Benitez, V.A. Mazzieri, C. Especel, F. Epron, C.R. Vera, C.L. Pieck, P. Marécot, *Catal. Commun.* 7 (2006) 627–632.
- [26] S.M. Agustine, W.M.H. Sachtler, *J. Catal.* 116 (1989) 184–194.
- [27] H. Lieske, G. Lietz, H. Spindler, J. Völter, *J. Catal.* 81 (1983) 8–16.
- [28] G. Lietz, H. Lieske, H. Spindler, W. Hanke, J. Völter, *J. Catal.* 81 (1983) 17–25.
- [29] V.M. Benitez, M. Boutzeloit, V.A. Mazzieri, C. Especel, F. Epron, C.R. Vera, P. Marécot, C.L. Pieck, *Appl. Catal.* 319 (2007) 210–217.
- [30] S.H. Cho, J.S. Park, S.H. Choi, S.H. Kim, *J. Power Sources* 156 (2006) 260–266.
- [31] B. Coq, F. Figueras, *J. Catal.* 85 (1984) 197–205.
- [32] F.H. Ribeiro, A.L. Bonivardi, C. Kim, G.A. Somorjai, *J. Catal.* 150 (1994) 186–198.
- [33] P. Biloen, F.M. Duatzenberg, W.M.H. Sachtler, *J. Catal.* 50 (1977) 77–86.
- [34] M. Boudart, A. Aldag, J.E. Benson, V.A. Dougharty, C.G. Harkings, *J. Catal.* 6 (1966) 92–99.
- [35] G.A. Mills, H. Heinemann, T.H. Milleken, A.G. Oblad, *Ind. Eng. Chem.* 45 (1953) 134–137.
- [36] J.M. Parera, N.S. Figoli, in: G.J. Antos, A.M. Aitani, J.M. Parera (Eds.), *Catalytic Naphtha Reforming*, 2nd edition, Marcel Dekker Inc, New York, 2004, pp. 75–104.
- [37] C.A. Querini, N.S. Figoli, J.M. Parera, *Appl. Catal.* 52 (1989) 249–262.
- [38] D.E. Sparks, R. Srinivasan, B.H. Davis, *J. Mol. Catal.* 88 (1994) 359–376.
- [39] J.M. Parera, N.S. Figoli, in: G.J. Antos, A.M. Aitani, J.M. Parera (Eds.), *Catalytic Naphtha Reforming: Science and Technology*, Marcel Dekker Inc, New York, 1995, pp. 45–78.