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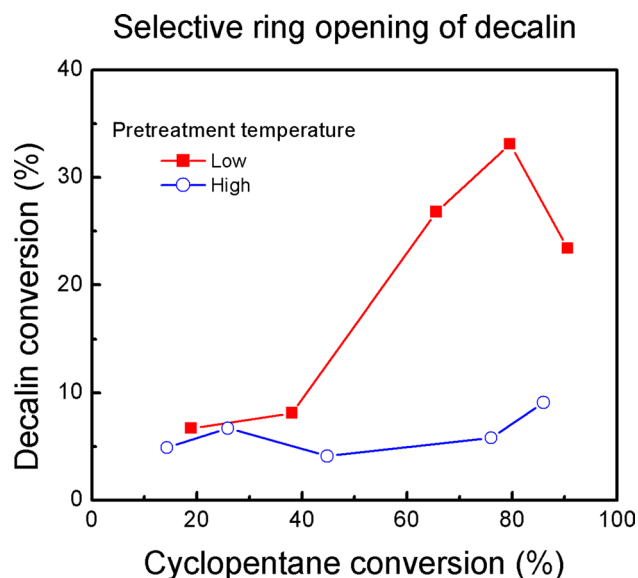
Pretreatment Temperature Influence on the Selective Ring Opening of Decalin on Pt–Ir/TiO₂ Catalysts

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Abstract In this work, the influence of the pretreatment conditions (calcination and reduction temperature) on the activity and selectivity of Pt–Ir/TiO₂ catalysts was studied. Two series of Pt–Ir/TiO₂ catalysts with a constant amount of Pt (1.0 wt%) and different Ir contents (0.3, 1.0 and 2.0 wt%) activated at different temperatures were prepared. The catalysts were characterized by TPR and test reactions such as cyclopentane and methylcyclopentane hydrogenolysis and cyclohexane dehydrogenation. The selective ring opening (SRO) performance of the catalysts was also evaluated on decalin. The catalysts activated by treatment at a lower temperature showed higher dehydrogenation and hydrogenolysis activity. Furthermore, they exhibited greater selectivity for ring opening products and reduced formation of dehydrogenated compounds. The activation treatment appears to be crucial, as it affects not only the activity, but the selectivity towards different reaction products.

Graphical Abstract



Keywords Selective ring opening · Titania · Pt–Ir · Pretreatment

1 Introduction

One promising alternative to increase the diesel output of a modern refinery is the selective ring opening (SRO) of light cycle oil (LCO), a byproduct of catalytic cracking (FCC). The challenge is to produce a fuel with high quality and low sulfur and aromatics contents in order to meet economic and health requirements [1]. Common diesel fractions do not fulfill the modern specifications applicable to diesel fuels due to the high content of polyaromatic compounds and naphthenes (48–70%) [2]. The classical hydrotreatment

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process can overcome some of these problems by eliminating oxygen, sulfur and nitrogen compounds. However, SRO improves diesel quality further, acting over cyclic compounds which represent a larger fraction [3]. Through this process, the cetane index is increased by converting polyaromatic compounds into alkanes (mainly linear alkanes) [4].

SRO research has been mainly focused on noble metals (such as Ir and Pt) supported on acidic materials to produce bifunctional catalysts, where acid and metal functions cooperate towards the endocyclic C–C breaking of naphthenes [5]. The acid sites promote both cracking (via β -scission mechanism) and isomerization reactions [6], while the metal catalyzes the hydrogenolysis and hydrogenation/dehydrogenation reaction steps [7]. SRO of 6-membered-ring compounds has been reported to occur over bifunctional catalysts containing well balanced metallic and acidic functions [8] through skeletal isomerization (i.e., ring contraction), which would also represent the limiting step of the whole SRO reaction system [9]. On the other hand, a direct ring opening pathway may be observed when the metal is supported on a non-acidic material [10, 11].

In a previous work, we studied Pt and Ir catalysts supported on TiO₂, Al₂O₃ and SiO₂ [12, 13]. The metal and the support were found to have a strong influence on the SRO of mono- and bicyclic naphthenics, being the catalysts supported on Al₂O₃ the most selective and active [13]. In that study, the catalysts supported on TiO₂ were activated by reduction at 450 °C. This treatment could have reduced the metal activity since TiO₂ exhibits strong metal support interactions (SMSI) developed during hydrogen treatment at high temperature [14–16]. Of course, the catalyst selectivity can also be modified by the influence of the support on the metal activity. For this reason, we decided to revisit the Pt–Ir catalysts supported on TiO₂ but using lower reduction temperatures in order to reduce the influence of SMSI.

2 Experimental

2.1 Support Preparation Method

The TiO₂ preparation method has previously been described [17]. Briefly, titanium tetrachloride (Merck, 99%) was dissolved in distilled water. The solution was acidified to pH 2 with concentrated HCl to promote hydrolysis. Then the aqueous solution was placed in a bath at 30 °C for 1 h and ammonia was used to set the pH at 10. The precipitated (TiO₂·nH₂O) was separated and washed with distilled water to remove excess chloride ions. The oxide was then dried at 110 °C for 12 h and calcined for 2 h at 500 °C under flowing dry air. The X-ray diffraction of the prepared TiO₂ mainly shows an anatase structure with some traces of a

rutile phase. The final pore volume was 0.8 cm³ g⁻¹ and the surface area, 80 m² g⁻¹.

2.2 Catalyst Preparation Methods

The catalyst preparation method was also described previously [13]. In short, the TiO₂ support was impregnated with an aqueous solution of metallic precursors (H₂PtCl₆ and H₂IrCl₆ from Sigma–Aldrich) in order to obtain metal loadings of 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. Then, the samples were kept at 70 °C until a dry solid was obtained. After that, the catalysts were heated in an oven at 120 °C for 12 h. Finally, the samples were calcined under flowing air for 4 h at 350 °C and were reduced in hydrogen during 4 h at 300 °C. Hereafter the catalysts are labeled Pt–Ir(x)-LT, where x denotes the content (wt%) of Ir, LT meaning low temperature pretreatment. A second series of catalysts from a previous work [13] was used with equal metal composition and prepared by the same procedure but activated at higher pretreatment temperature (calcination at 500 °C and reduction at 450 °C) denoted Pt–Ir(x)-HT.

2.3 Evaluation of the Pt, Ir and Cl Contents

The metal load was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution and dilution. The chlorine content was determined spectrophotometrically by the mercury thiocyanate method using a Metrolab 1700 Spectrophotometer.

2.4 Temperature-Programmed Reduction (TPR)

The experiments were performed in a quartz reactor charged with a 200 mg sample. The samples were calcined in air at 350 °C for 1 h. They were then cooled with air down to room temperature. Finally the temperature was raised to 700 °C with a heating rate of 10 °C min⁻¹ using a mixture of H₂ (5% v/v)–N₂ (9 cm³ min⁻¹). The reactor outlet was connected to an online TCD to determine the outlet hydrogen concentration.

2.5 Temperature-Programmed Desorption of Pyridine (TPD)

The procedure has been previously reported [12]. In summary, the catalyst was impregnated with pyridine (Merck, 99.9%) at room temperature and the weakly physisorbed pyridine was desorbed by heating the sample at 110 °C for 1 h in a N₂ flow (40 cm³ min⁻¹). Then, the temperature was raised to 600 °C at heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a FID.

2.6 Transmission Electron Microscopy (TEM)

Transmission electron micrographs (TEM) were obtained in a JEOL100 CXII microscope. The supported catalysts were ground in an Agatha mortar and dispersed in ethanol. A diluted drop of each dispersion was placed on a 150 mesh carbon-coated copper grid. The mean particle diameter (d_p) was calculated as:

$$d_p = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2}$$

where n_i is the number of particles of diameter d_i .

2.7 Test Reactions

The catalysts were characterized by means of test reactions: cyclohexane (CH) dehydrogenation, cyclopentane (CP) hydrogenolysis and methylcyclopentane ring opening. The reaction conditions were reported by Vicerich et al. [13] but, as previously stated, the catalysts were reduced at a lower temperature. For the sake of simplicity, Table 1 shows the reaction conditions used.

2.8 Decalin Ring Opening (RO)

The experimental conditions, chromatographic analysis and the equipment used were reported before [13]. The reaction conditions were: temperature = 325 °C, hydrogen pressure: 3 MPa, stirring rate = 1360 rpm, volume of decalin = 25 cm³, catalyst loading = 1 g and reaction time = 6 h.

3 Results and Discussion

The preparation method yielded inhomogeneous catalysts with correct metal deposition and strong metal interactions. On one hand, metal contents obtained through ICP-OES chemical analysis were found to be in good agreement with the expected theoretical values for all samples (results not shown). On the other hand, TPR profiles of the bimetallic

Table 1 Reaction conditions

	CH dehydrogenation	CP hydrogenolysis	MCP ring opening
Reaction temperature (°C)	300	300	250
Mass of catalyst (mg)	50	150	135
WHSV (h ⁻¹)	11.3	2.4	2.0
H ₂ /HC	14.3	20.7	29.9
Pretreatment temperature (°C)	300	300	250

catalysts presented broad reduction peaks with its temperature between those of the monometallic Pt and Ir catalysts. The reduction temperature was found to increase at higher Ir loads (Fig. 1). This behavior suggests that the metallic phase contains Pt–Ir ensembles or at least Pt and Ir species in strong interaction. The width of the reduction peaks, that appear broader at higher metallic loads, can be explained by inhomogeneous interaction between Pt and Ir species with the support and/or metallic particle size distribution [18]. As was previously reported [13], the Pt–Ir(2.0)-HT catalyst presented a unique reduction profile with a pair of peaks around 205 and 291 °C. These peaks were attributed to the presence of Pt-rich and Ir-rich Pt–Ir ensembles, respectively, or to the presence of segregated iridium species [13].

The higher temperature treatment was found to produce slight sintering. The particle size distribution of the Pt(1.0)–Ir(x)/TiO₂ catalysts obtained by TEM and represented in Fig. 2 clearly shows that the higher temperature treatment increases particle sizes in agreement with previous results [12]. Also, the catalysts with a higher metal load presented a higher metal particle size. The mean particle size diameter changes from 1.3 to 1.4 nm for Pt–Ir(1.0) catalysts and from 1.3 to 1.5 nm for Pt–Ir(2.0) catalysts when the pretreatment temperature changes from 300 to 450 °C. The differences are small enough to suppose they have no major impact on the activity of the catalysts.

Another consequence of the higher temperature during reduction is a decrease in the acidity of the support.

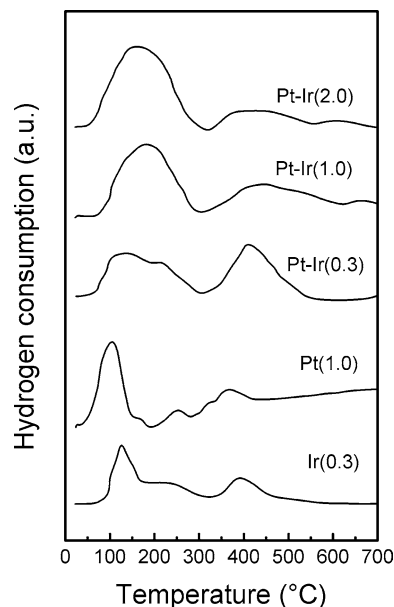


Fig. 1 Temperature programmed reduction profiles of the Pt–Ir(x)/TiO₂-LT catalysts. Signal of Ir monometallic catalysts multiplied by three

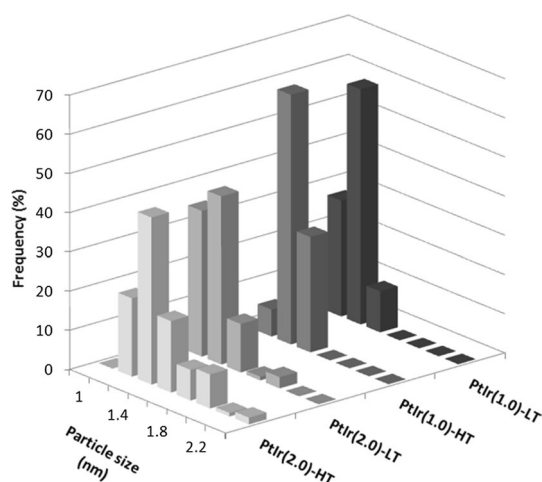


Fig. 2 Particle size distribution obtained by TEM of the bimetallic catalysts

Figure 3 shows the total acidity determined by pyridine desorption as a function of the chlorine content of the catalysts. The total acidity values were obtained by integration of the pyridine TPD profiles. It can be observed that the LT series of catalysts exhibited a higher total acidity and chlorine content than the HT catalysts. The lower acidity of the catalysts treated at a higher temperature could be due to the elimination of chlorine produced during the calcination and reduction steps used in the preparation of the catalysts (chlorine leaching). Cl⁻ ions are known to boost the acidity of OH groups by inductive effects [19–21]. The elimination of chlorine during the calcination and reduction pretreatment has been also reported for naphtha reforming catalysts

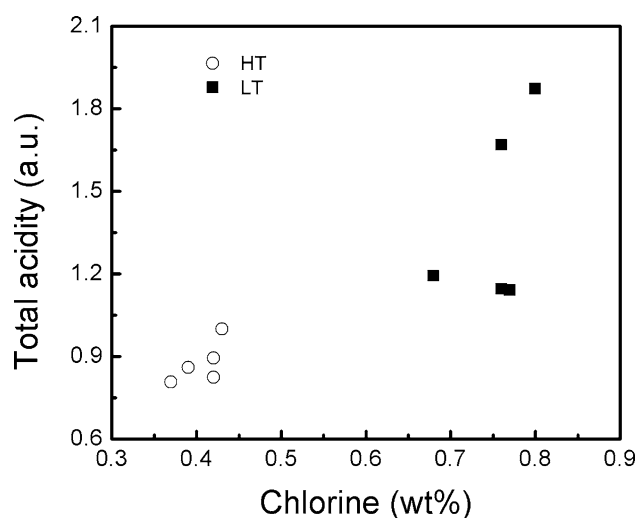


Fig. 3 Total acidity determined by pyridine desorption as a function of chlorine of the catalysts

(Pt/Al₂O₃ and Pt–Re/Al₂O₃) [22, 23]. There seems to be no clear correlation between the total acidity and Ir content.

According to TPR results, catalysts treated at a higher temperature would have also endured partial reduction of the support, the first step of the SMSI phenomenon. A reduction zone between 300 and 600 °C is observed in all TPR profiles. Under these conditions, TiO₂ can migrate and cover the metal particles [14, 15, 24]. The electronic properties of the metals are strongly modified by their interaction with the surface TiO₂ species [25]. These interactions are favored by high temperatures during the reduction treatment [26].

Different test reactions were used in order to discriminate the kind of influence the SMSI effect had on the Pt–Ir ensembles. As described in the “Experimental” section, cyclohexane dehydrogenation, cyclopentane hydrogenolysis, methylcyclopentane and decalin ring opening tests were performed. Cyclohexane dehydrogenation is a typical non-demanding reaction, where the catalyst activity is directly proportional to the number of metal atoms available on the surface [27, 28]. As shown in Table 2, the dehydrogenation activity of monometallic Pt catalysts is higher than the monometallic Ir catalysts for both series in agreement with previous reports [29]. On the contrary, cyclopentane hydrogenolysis is a demanding reaction, and requires a specific ensemble of atoms [30]. Table 2 shows that monometallic Ir catalysts have a higher hydrogenolytic activity than Pt catalysts for both series in agreement to previous results [31]. Moreover, Fig. 4 shows that the conversion of cyclopentane increases linearly with the cyclohexane conversion, except in the case of the monometallic Pt catalysts. Methyl-cyclopentane ring opening allows determining if ring opening occurs either through a selective or non-selective mechanism, or a mixture of both. Finally, decalin SRO is a complex reaction with a large amount of possible byproducts and provides information on selectivity towards SRO products compared to cracking or dehydrogenation products. The effect of the acid function is also not

Table 2 Cyclohexane and cyclopentane conversion (%) of the Pt–Ir(x)/TiO₂ catalysts treated at high temperature (HT) and low temperature (LT)

Catalyst	Cyclohexane		Cyclopentane	
	HT	LT	HT	LT
Pt(1.0)	23.0	33.3	14.3	18.9
Pt–Ir(0.3)	40.9	48.3	44.8	65.6
Pt–Ir(1.0)	52.5	56.1	76.0	79.6
Pt–Ir(2.0)	68.8	74.5	86.0	90.6
Ir(0.3)	17.8	24.1	25.9	38.1

Pretreatment temperature before reaction 300 °C

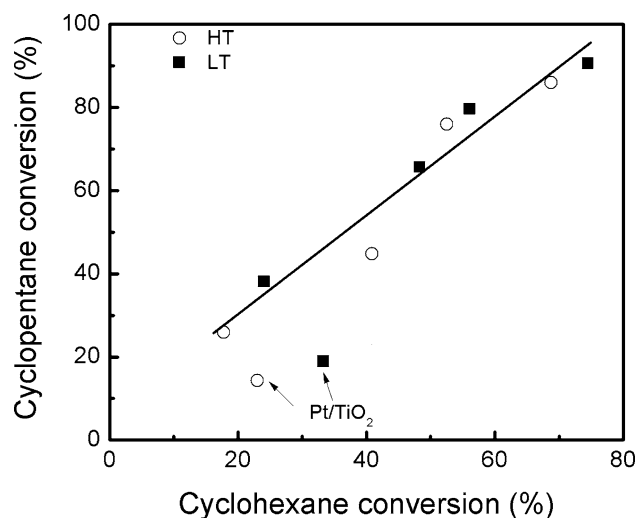


Fig. 4 Cyclopentane conversion as a function of cyclohexane conversion

Table 3 Conversion, selectivity to ring opening and molar ratio of $nC_6/3MP$ and $2MP/3MP$ obtained after 15 min time on stream of methylcyclopentane

Catalyst	Conversion	Selectivity to RO	$nC_6/3MP$	$2MP/3MP$
Pt(1.0)-LT	4.2	72	2.92	2.08
Pt-Ir(0.3)-LT	43.8	81	0.55	1.23
Pt-Ir(1.0)-LT	62.8	85	0.85	1.21
Pt-Ir(2.0)-LT	77.4	80	0.33	1.33
Ir(0.3)-LT	8.8	79	0.7	1.74

negligible since ring contraction over acid sites (from 6 to 5 carbon rings) promotes latter ring opening.

The SMSI effect was found to reduce the metal activity of the catalyst regardless of the catalyst and test reaction studied. Conversely, the highest metal activity was found on the catalysts activated at a lower temperature.

Comparing the activity of bimetallic catalysts is not straightforward since the metallic load varies depending on the composition. Because of this, in the case of cyclohexane dehydrogenation and cyclopentane hydrogenolysis, the activity of the bimetallic catalysts is higher than the activity of either monometallic catalyst but also because of the formation of Pt-Ir ensembles [30]. However, the comparison between LT and HT catalysts is direct. In all cases, the metal activity was found to be higher for LT catalysts. This could be caused in part by the higher metallic dispersion of the LT-series catalysts (Fig. 2). The negative impact of the SMSI effect at higher temperatures ($>500^\circ C$) has already been reported [14, 16]. The importance of the SMSI effect can be evaluated by comparing the cyclohexane dehydrogenation and cyclopentane hydrogenolysis performance of

the LT-series catalysts shown in Table 2 to previously published results for the HT-series [13]. Since both test reactions occur on different sites and through different mechanisms, it is reasonable to say that the overall tendency shown represents the metal activity of the catalysts.

The SMSI effect has a similar impact on the methylcyclopentane yield of ring opening products (cf. Table 3). In these tests, Ir catalysts are more active than Pt catalysts and the activity of bimetallic catalysts increases with the Ir load. Again, the negative SMSI effect reduces the activity of the HT series (data from [13]) compared to the LT series.

Maire et al. [32] proposed three reaction mechanisms for methylcyclopentane over metallic catalysts. According to them, a non-selective reaction path can occur over the metal and would present the same breaking probability for any of the cyclic bonds, yielding a product ratio n -hexane/2-methylpentane/3-methylpentane ($nC_6:2MP:3MP$) of 2:2:1. On the other hand, a selective reaction path can occur in which only bissecondary C-C bonds are broken, with a product ratio $nC_6:2MP:3MP$ of 0:2:1. Since experimental results could not be explained by a combination of these two mechanisms, they proposed a third mechanism, the partially selective mechanism. The reaction can also be catalyzed by acid sites [5], favoring ring opening of bonds adjacent to the methyl group. In all tests, the $nC_6/3MP$ ratio was between 0.5 and 0.85 while the $2MP/3MP$ ratio was between 1.21 and 1.74, except for the monometallic Pt(1.0)-LT catalyst which shows $nC_6/3MP$ and $2MP/3MP$ ratios of 2.92 and 2.08, respectively. These values indicate that the partially selective mechanism is present. The higher $nC_6/3MP$ ratio found for Pt(1.0)-LT catalyst could be due to an increase on the acid mechanism contribution due the lower hydrogenolytic activity of Pt compared to Ir.

Figure 5 shows the methylcyclopentane conversion and yield to ring opening products as a function of cyclopentane conversion, thus comparing the SRO and hydrogenolytic activity of the catalysts. It can be observed that there is a linear correlation between the two variables, excluding once more monometallic Pt catalysts. The same linear correlation can be found between the SRO and dehydrogenation activity of the catalyst (results not shown). Hence, the SRO selectivity and activity are proportional to the metal activity, independently of the activation treatment. Furthermore, it can be concluded that the influence of the activation temperature on these reactions is due to the SMSI effect.

Another aspect that should be taken into account is the effect of the reduction temperature on the acidity of the support. Decalin SRO can be promoted purely by the metal sites, but a prior ring contraction from a 6-membered ring to a 5-membered ring catalyzed over an acid site can greatly increase the reaction rate [5]. Thus, the combined

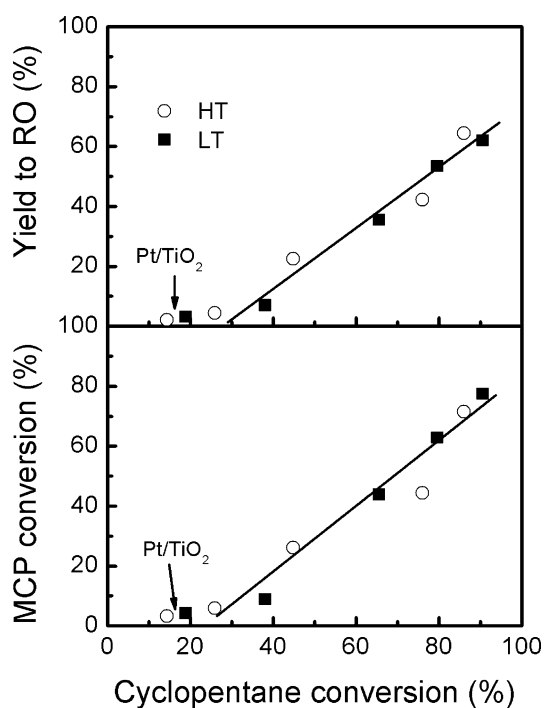


Fig. 5 Methylcyclopentane conversion and yield to ring opening products (RO) as a function of cyclopentane conversion

effect of the lower acidity of the HT series (Fig. 3) and the SMSI effect explains the low conversion values obtained for decalin at 6 h of reaction compared to the LT series (cf. Table 4). The lower acidity also explains the non-proportionality between the activity of the HT and LT series for decalin (Fig. 6), in contrast with the results found for hydrogenolysis and dehydrogenation. In general, HT catalysts exhibited a high selectivity towards dehydrogenated products, with monometallic Ir achieving a surprisingly high value [13]. Given the low acidity of these catalysts, dehydrogenation over the metal function becomes the primary reaction path. Selectivity to cracking products is higher on the bimetallic catalysts given the high hydrogenolytic activity of Ir.

Table 4 Conversion and selectivity obtained in the reaction of decalin

Catalyst	Conversion (%)	Selectivity (%)			
		RO	DH	PC	RC
Pt(1.0)-LT	6.7	49.5	13	0	37.5
Pt–Ir(0.3)-LT	26.8	45.1	39.7	5.03	10.8
Pt–Ir(1.0)-LT	33.1	71.9	4.5	10.2	13.4
Pt–Ir(2.0)-LT	23.4	69.4	9.6	15.7	5.3
Ir(0.3)-LT	8.1	20.1	61.3	0	18.6

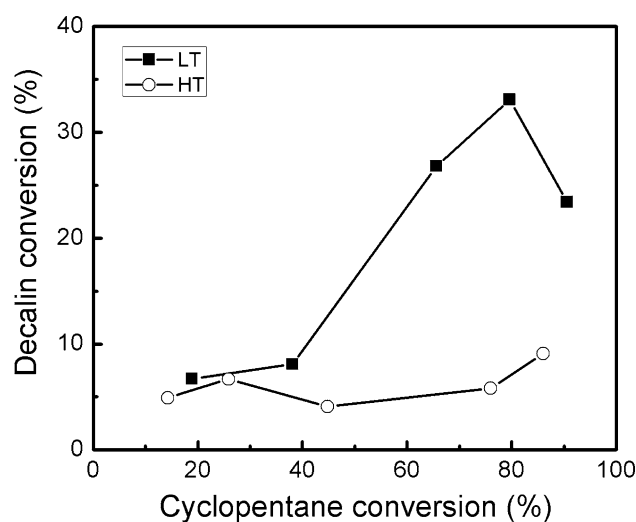


Fig. 6 Decalin conversion as a function of cyclopentane conversion

With an improved metal–acid balance, the LT catalysts had a higher selectivity towards ring opening products and a reduced formation of dehydrogenated products. Increasing the Ir loads does improve SRO performance but only up to a certain point. Figure 6 shows that the Pt(1.0)–Ir(2.0)-LT catalyst, exhibiting the highest hydrogenolytic activity (cyclopentane conversion), does not deliver the highest decalin conversion, achieved instead by the Pt(1.0)–Ir(1.0)-LT catalyst. This may be linked to the fact that Pt–Ir ensembles in this catalyst were found to be divided into two groups according to TPR results (Fig. 1), one of which may be more active to promote this reaction.

The higher sensibility of the decalin ring opening reaction compared to the methylcyclopentane (MCP) reaction to the activation treatment could be due to decalin RO proceeding by a bifunctional mechanism involving the acid and metal sites. MCP RO can also be promoted by an acid mechanism, but is mainly catalyzed by the metal sites, since there is no ring contraction required. Therefore, the MCP yield to RO products is a linear function of the metal activity (measured as cyclopentane conversion) as can be seen in Fig. 5.

Finally, it is interesting to compare the effect of the support on decalin SRO. Table 5 shows the performance of Pt–Ir catalysts supported on TiO₂, SiO₂ and Al₂O₃. The Pt–Ir(1.0)/TiO₂-LT catalyst has a higher conversion and selectivity to RO products than catalysts supported on Al₂O₃ and SiO₂ with an equivalent metal load. With an adequate thermal treatment, it is possible to express the full catalytic potential of the catalysts supported on TiO₂. Lower reduction temperatures produces less chlorine leaching and the SMSI effect is limited. As a consequence, the catalysts have adequate bifunctional properties.

Table 5 Conversion of decalin and selectivity to RO products reported using different catalysts at the same reaction conditions

Catalyst	Conversion (%)	Selectivity to RO (%)	References
Pt–Ir(1.0)-LT	33.1	71.9	This work
Pt–Ir(1.0)-HT	5.8	46.1	Vicerich et al. [13]
Pt–Ir(1.0)/Al ₂ O ₃	9.5	65.9	Vicerich et al. [13]
Pt–Ir(1.0)/SiO ₂	7.7	3.7	Vicerich et al. [13]

4 Conclusions

Pt–Ir catalysts supported on TiO₂ prepared by coimpregnation exhibited strong Pt–Ir interactions, independently of the activation temperature. However, the interaction between the metal and the support are stronger in the case of the LT catalysts.

Cyclohexane dehydrogenation and cyclopentane hydrogenolysis test reactions proved that the metal activity increased with the metal charge. In addition, a strong influence of the activation temperature on the activity of the metal function was found. High temperatures promote the migration of TiO_x (x < 2) species towards Pt and Ir ensembles, decreasing their activity by a geometric effect (blocking) or alteration of the electronic properties of the active metals.

These results indicate that treatment activation of the catalysts is important because changes its activity and selectivity.

The results of decalin and methylcyclopentane ring opening tests showed that the (mainly bimetallic) LT catalysts are more active than the HT activated catalysts. Furthermore, the selectivity to desired products (ring opening products) is greater in the LT series.

References

- Galadima A, Muraza O (2016) *Fuel* 181:618
- Lü XC, Yang JG, Zhang WG, Huang Z (2005) *Energy Fuels* 19:1879
- Heidari A, Hashemabadi SH (2015) *Chem Eng Res Des* 94:549
- Santana RC, Do PT, Santikunaporn M, Alvarez WE, Taylor JD, Sughrue EL, Resasco DE (2006) *Fuel* 85:643
- Du H, Fairbridge C, Yang H, Ring Z (2005) *Appl Catal A* 294:1
- Kubicka D, Kumar N, Mäki-Arvela P, Tiitta M, Niemi V, Salmi T, Murzin DY (2004) *J Catal* 222:65
- Shi H, Li X, Haller GL, Gutiérrez OY, Lercher JA (2012) *J Catal* 295:133
- Santi D, Holl T, Calemma V, Weitkamp J (2013) *Appl Catal A* 455:46
- Figueras F, Coq B, Walter C, Carriat JY (1997) *J Catal* 169:103
- McVicker GB, Daage M, Touvelle MS, Hudson CW, Klein DP, Baird WC, Cook Jr BR, Chen JG, Hantzer S, Vaughan DEW, Ellis ES, Feeley OC (2002) *J Catal* 210:137
- Haas A, Rabl S, Ferrari M, Calemma V, Weitkamp J (2012) *Appl Catal A* 426:97
- Vicerich MA, Benitez VM, Especel C, Epron F, Pieck CL (2013) *Appl Catal A* 453:167
- Vicerich MA, Benitez VM, Sanchez MA, Pieck CL (2015) *Catal Lett* 145:910
- Ekou T, Ekou L, Vicente A, Lafaye G, Pronier S, Especel C, Marécot P (2011) *J Mol Catal A* 337:82
- Alonso F, Riente P, Rodríguez-Reinoso F, Ruiz-Martínez J, Sepúlveda-Escribano A, Yus M (2008) *J Catal* 260:113
- Tauster SJ, Fung SC (1978) *J Catal* 55:29
- Benítez VM, Yori JC, Vera CR, Pieck CL, Grau JM, Parera JM (2005) *Ind Eng Chem Res* 44:1716
- Carnevillier C, Epron F, Marécot P (2004) *Appl Catal A* 275:25
- Gates BC, Katzer JR, Schuit AGC (1979) *Chem of Catal Proc*. McGraw-Hill, New York
- Melchor A, Garbowski E, Mathieu M, Primet MJ (1986) *Chem Soc Faraday Trans I* 82:1893
- Carvalho LS, Pieck CL, Rangel MC, Fígoli NS, Vera CR, Parera JM (2004) *Appl Catal A* 269:105
- Bishara A, Murad KM, Stanislaus A, Ismail M, Hussain SS (1983) *Appl Catal* 7:337
- Grau JM, Jablonski EL, Pieck CL, Verderone RJ, Perera JM (1988) *Appl Catal* 36:109
- Hayek K, Kramer R, Pafil Z (1997) *Appl Catal A* 162:1
- Tauster SJ, Fung SC, Garten RL (1978) *J Am Chem Soc* 100:170
- Poondi D, Vannice MA (1997) *J Mol Catal A* 124:79
- Frank JP, Martino G (1982). In: Figueiredo J (eds) *Progress in catalyst deactivation*. Martinus Nijhoff, The Hague, p 355
- Carvalho LS, Pieck CL, Rangel MC, Fígoli NS, Grau JM, Reyes P, Parera JM (2004) *Appl Catal A* 269:91
- Benitez VM, Boutzeloit M, Mazzieri VA, Especel C, Epron F, Vera CR, Marécot P, Pieck CL (2007) *Appl Catal A* 319:210
- Gault FG (1981) *Adv Catal* 30:1
- Davis BH (1999) *Catal Today* 53:443
- Maire G, Plouidy G, Prudhomme JC, Gault FG (1965) *J Catal* 4:556