



Promising PtIr, catalysts for hydrocarbon transformation: Comparison of different preparation methods

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ABSTRACT

Ir–Pt/Al₂O₃ catalysts were prepared by adding Ir to Pt catalysts using two methods: successive impregnation (SI) or organometallic grafting (OG). These resulted in different structures: with the first method (SI) Pt and Ir sites were separated, whereas bimetallic Pt–Ir sites are created by the second method (OG), as demonstrated also by electron microscopy. We tested the bimetallic catalysts obtained by these two preparation methods using hydrocarbon transformation, particularly the reaction of ring opening of methylcyclopentane (MCP). The OG catalyst shows a very promising behavior in ring opening reaction of MCP, showing high activity and producing ring opening products (ROP) with high selectivities even at high conversion values.

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1. Introduction

Reforming of hydrocarbons is an important catalytic process for the production of high-octane gasoline, aromatics and hydrogen from naphtha. The reactions involved in this process are hydrogenation, dehydrogenation, isomerization, cyclization and hydrogenolysis or hydrocracking.

During naphtha reforming, a complex reaction network takes place which includes both desired and undesired reactions. The desired transformations are dehydrogenation of naphthenes, isomerization and dehydrocyclization of alkanes. Undesired reactions are the hydrogenolysis and the cracking of alkanes that produce light hydrocarbons of negligible value and decrease the overall liquid C₅ + yield. Coking is another secondary reaction, the rate of which needs to be decreased in order to prevent the premature deactivation of the catalyst by the accumulation of carbonaceous deposits on the active sites. It is widely accepted that the hydrogenation–dehydrogenation reactions occur over the metallic sites of the catalyst while isomerization and dehydrocyclization proceed mostly on bifunctional metal–acid sites, the mechanism being controlled by the acidic function. For this reason, the naphtha reforming catalysts has to possess two catalytic functions. The metallic function

is usually provided by Pt in the form of very small particles dispersed on the surface of the catalyst. Its properties can be fine-tuned by the addition of another element, the so-called metal function promoter that can be another noble metal, e.g. Ir, or another element with the desired properties (Sn, Ge). The acidic function is provided by the support itself. In most applications is γ -Al₂O₃ treated with chlorine in order to increase its surface acidity.

Several bimetallic catalysts have been the subject of research studies, and some have also found applications in practice [1,2]. Nowadays, an increased attention has been paid to preparation methods using “Controlled Surface Reactions (CSR)” [3,4], even though industrial bimetallic catalysts are usually prepared by simple methods, such as co-precipitation or co-impregnation. Therefore, our aim was to investigate bimetallic Pt–Ir catalysts prepared by two different methods, namely by classical successive impregnation and by organometallic grafting [3,5]. These catalysts are rather active and selective in various reactions, e.g., in hydrocarbon transformations [4,5], which could lead to promising results in cleaner products and safer processes producing less waste.

Several papers have dealt with the catalytic reaction of methylcyclopentane (MCP) on platinum [6,7] because the ring opening can be seen as a peculiar C–C rupture. Two types of reactions were observed on MCP. A non-selective ring opening cleaves each C–C

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bond in a random way. This phenomenon is reported with a high dispersion of Pt [8]. A selective splitting takes place on larger Pt particles, breaking C–C bonds in β and γ positions with respect to the methyl group, producing 2-methylpentane (2MP) and 3-methylpentane (3MP), respectively. The ratio 2MP/3MP from MCP conversion is close to the statistical value of 2 on most Pt and Rh catalysts [6]. The selective ring opening was interpreted by assuming a “flat-lying” intermediate [9].

We have to notice that the H_2 pressure is important in the activity and the selectivity of the reaction of ring opening (RO). The RO reaction becomes the main reaction with the increase of H_2 pressure. And when the H_2 pressure is low, the forming of olefins is favored [10].

The use of Ir permits to obtain active catalysts for the RO reaction, at a temperature from 423 K. Gault et al. [11] have supposed the existence of a common intermediate for the ring opening and the ring closure reactions. Furthermore, they have shown that isomerization $2MP \rightleftharpoons 3MP$ is possible, without *n*-hexane formation. van Senden et al. [12] have found that carbonaceous deposits on the surface affect the RO. Virgin surfaces promote an evidently selective RO, with an almost total absence of hexane. Surfaces with increasing amount of carbonaceous deposits show an increasing tendency to a non-selective RO, with appreciable amounts of hexane. Very similar effect has been found on Pt/SiO₂ catalyst [14]. It has been observed that the RO does not depend on the dispersion, but the smaller particles show a higher resistance against self-poisoning by the carbonaceous deposits than the larger ones. Selective opening of the cyclopentane ring took place on four metals: Pt, Pd, Ir and Rh [13]; Ir, Rh being more active in C–C bond breaking than Pt, Pd.

If the ratio H_2 /MCP decreases [15], the rate of the reaction increases to reach a maximum and then it decreases. When we decrease the H_2 pressure, the ratio 2MP/*n*H also decreases, which shows that selective rupture is the most important reaction.

Pt–Ir catalysts show a marked increase in hydrogenolysis activity. This is attributed to the presence of metallic Ir [16]. This catalyst presents a very slow deactivation, attributed to the ability of iridium to prevent coke formation on the metal by hydrogenolysis/hydrogenation of coke fragments or the precursors of coke.

In the present work, Pt–Ir/Al₂O₃ catalysts prepared by grafting or successive impregnation were studied in the hydrogenolytic ring opening (ROP) reaction of methylcyclopentane. They were characterized by H_2 chemisorption and transmission electron microscopy (TEM). Our aim was to discover differences between the structure of the catalysts and the observed activity pattern.

2. Experimental

The 1 wt.% monometallic parents catalysts were prepared by wet impregnation of alumina from Degussa ($100 \text{ m}^2 \text{ g}^{-1}$) with salts of platinum [Pt(NO₂)₂(NH₃)₂] or iridium [Ir(acac)₃]. The impregnated support was left overnight in an oven at 393 K. It was then calcined in dry air at 773 K for 4 h and reduced in N₂ flow containing 20% H_2 for 4 h at 773 K. Dispersion was 50%, as determined by H_2 chemisorption.

Different bimetallic catalysts were prepared by using successive impregnation or the surface organometallic chemistry method [5,17]. For the successive impregnation, the Pt parent was impregnated with the Ir precursor [Ir(acac)₃]. Then it was calcined in dry air at 673 K for 3 h and reduced in N₂ flow containing 20% H_2 for 3 h at 673 K [17,18]. The samples were denoted as PtIr(SI).

The second method used for the preparation of the Pt–Ir catalyst was the organometallic grafting. In this case, 6.61 g of the parent Pt sample was pre-reduced (in H_2 flow at $T = 673 \text{ K}$ for 2 h, heating rate 2 K/min), cooled in H_2 to room temperature and kept

at room temperature for 1 h (H_2 adsorption). It was first immersed in 15 ml toluene, then 15 ml toluene solution of Ir(acac)₃, purity min 37.5%, was added, and kept for 6 h at 343 K in bubbling Ar. The amount of Ir(acac)₃ dissolved in toluene corresponded to nominal coverage of 1/2 Ir monolayer, as calculated for surface Pt atoms. The samples were washed with toluene and dried in Ar flow at 393 K for 1 h. They were finally reduced in H_2 flow (473 K; 4 h). This reduction temperature was found to be sufficient for producing catalytically active and reproducible samples [17,19,20]. The samples were denoted as PtIr(OG). The final metal content was experimentally determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) after dissolution of the samples.

Transmission electron microscopy was used to estimate the particle size and provide information on the components. The catalyst samples were ground in an agate mortar, then dispersed in ethanol and dropped onto holey carbon grid. For conventional TEM studies, a Philips CM20 electron microscope was used, at 200 kV accelerating voltage. This microscope was capable of carrying out Energy Dispersive X-ray Spectrometric (EDS) analysis on thin specimens with the attached X-ray detector. A high-resolution electron microscope of the type JEOL 3010 (working at 300 kV and supplemented with a GATAN Tridiem energy filter) was also applied for high-resolution imaging [22]. This equipment is suitable for acquiring images using electrons of specific energy losses (Energy Filtered TEM, EFTEM) creating thus so-called elemental maps [22]. The Pt M edge was used for elemental mapping with the three energy windows of 60 eV slit width each, centered at 2152 eV (post-edge), 2022 eV (pre-edge1) and 2082 eV (pre-edge2). The values for Ir M edge are 60 eV slit width, 2070 eV (post-edge), 1940 eV (pre-edge1) and 2000 eV (pre-edge2).

Catalytic experiments were carried out in a closed-loop apparatus connected to a CP 9001 gas chromatograph equipped with a 50-m CP-Sil 5CB capillary column and FID detector [5,17,21–24]. The MCP pressure was 10 Torr (1 Torr = 0.133 kPa), and the hydrogen pressure was varied between 120 and 480 Torr. The reaction temperatures ranged from 468 to 513 K. Sampling took place after 5 min. Regeneration between runs was carried out with 30 Torr air for 2 min followed by evacuation and 3 min of hydrogen treatment at 100 Torr. Activity and selectivity values on the regenerated samples were reproducible [25]. Furthermore, the oxidation effect and the reduction effect were studied. For the oxidation effect, before the series, the catalyst was oxidized at 603 K with 100 Torr of air for 30 min. Between the runs, the catalyst is only oxidized under the conditions cited before for regeneration. For the reduction effect, before the series, the catalyst was reduced at 603 K with 400 Torr of hydrogen for 1 h. Between the runs, the catalyst was only reduced under the conditions cited before for regeneration. Methylcyclopentane contained traces of hexane, which was taken into account when the product composition was calculated. The turnover frequencies were calculated as the number of MCP reacted per surface Pt atoms, as determined by H_2 chemisorption, using the length of the run as contact time [22].

3. Results and discussion

Pt–Ir/Al₂O₃ catalysts prepared by grafting or successive impregnation were studied in the hydrogenolytic ring opening reaction of MCP. In this study, we present evidence to establish that the structure of the PtIr(SI) is different to that of PtIr(OG).

3.1. Catalyst characterization

The monometallic catalysts had the same chemisorption values. These values are confirmed by the TEM study. That means that the

Pt catalyst was homogeneous. The same values between TEM and H_2 chemisorption for the Ir catalyst ensured the hypothesis, $1Ir_s = 1H_{ads}$, used for the chemisorption.

Some important results have been summarized in Table 1. The amounts of Pt and Ir, respectively, were close to the expected values on monometallic catalysts. The Ir percentage was lower than expected with OG preparation method: some of Ir may have been in positions not accessible by ICP. The PtIr(SI) should have dispersion higher than 50%, but the measurement showed a slight decrease. That can have two explanations: (i) the second calcination may have induced an enlargement of the metal particles; (ii) an alloy could be formed which chemisorbed less hydrogen than the monometallic parent catalysts. These explanations do not exclude each other and present experimental evidences cannot permit to select between these possibilities. Much larger drop of the amount of accessible Pt was found after the OG preparation. As TEM results exclude sintering of Pt crystallites, we can assume that the presence of Ir on Pt ensembles induced this special adsorption pattern. Carbonaceous residues from decomposing organometallic Ir complex may have remained on the metal surface and generated a poisoning effect [25]. These assumptions are in agreement with the presence of Ir on Pt particles, as evidenced EFTEM studies. Fig. 1 shows electron microscopic pictures of the PtIr(OG) catalyst.

Metal particles up to 20 nm (larger than the average) have been selected (arrows). Pt and Ir appear on the same areas in the EFTEM pictures. No such PtIr bimetallic particles were found on PtIr(SI), although the number of particles studied was below the amount necessary for quantitative statistics.

3.2. Catalytic reactions of MCP

3.2.1. Effect of hydrogen pressure and temperature

TOF was measured from time-averaged data. Very little selectivity changes appeared in a long test run between 5 and 80 min reaction times, thus we can exclude an important effect of deactivation or aging of catalysts. So, TOF reflects mainly the intrinsic activity. All catalysts had an increase in the TOF with the increase in temperature (Table 2) or the increase in hydrogen pressure (Table 3) or both of them. Monometallic catalysts showed different activities and selectivities. As opposed to high-pressure experiments [26], the Pt/ Al_2O_3 catalyst had markedly higher TOF values than Ir/ Al_2O_3 . Pt produced mainly ROP, except for the lowest hydrogen pressure (8 kPa), where benzene was the main product, due, likely, to thermodynamic reasons [27]. This low hydrogen pressure favored benzene formation (by ring expansion followed by dehydrogenation). Fragments and olefins formed as side prod-

Table 1

The main properties of catalysts by nominal content of Pt and Ir.

Catalysts	% of metal		Accessible Pt (%) expected	Accessible Pt (%) measured ^a	Particle size (nm)	
	Theoretical	ICP			TEM	H_2 ads
Pt	1	0.987	50	50	2.2	1.87
Ir	0.25	0.188	50	50	–	1.84
PtIr(SI)	0.2 of Ir	0.169 of Ir	>50	40	3.4	2.4
PtIr(OG)	0.246 of Ir	0.118 of Ir	~50	^b	3	^b

^a Calculated upon the number of accessible Pt using cubic particles model (five accessible faces and one hidden by the support).

^b The value given by H_2 chemisorption gave that the value of accessible Pt was lower than 50%, thus the calculated particle size was higher (up to 8 nm). This value contradicted to TEM, thus we attributed this discrepancy to the presence of chemisorbed carbonaceous residues from the decomposing organic Ir complex.

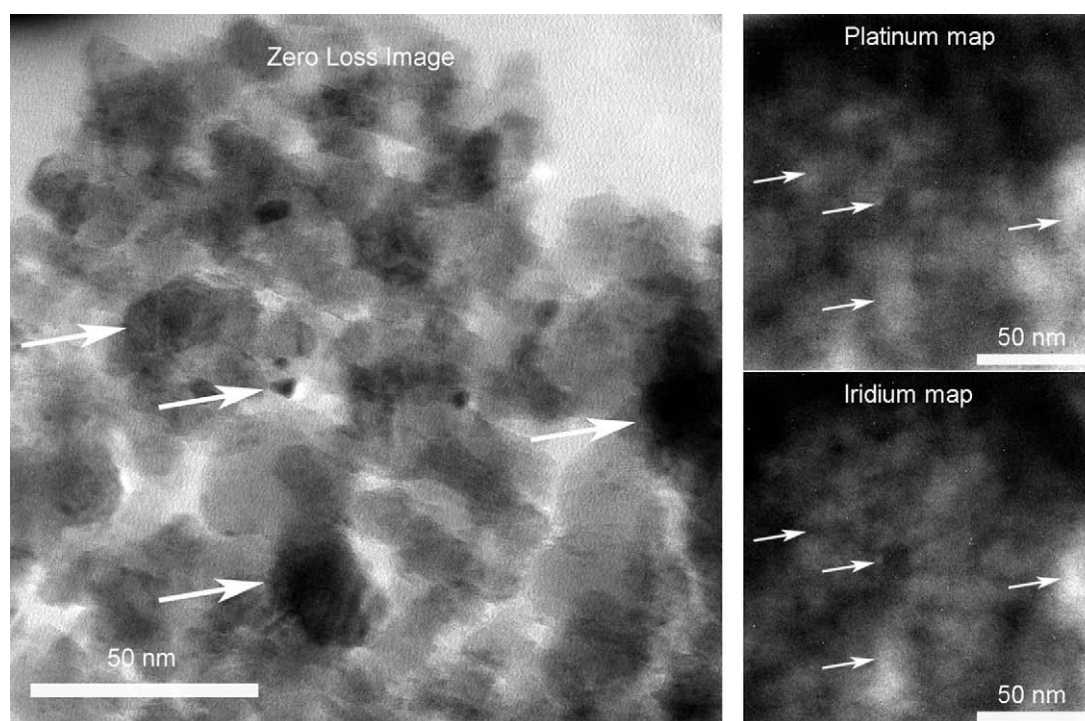


Fig. 1. TEM picture of the PtIr(OG) catalyst. Dark spots (denoted by arrows show likely metal particles (left-hand panel). The other two panels show EFTEM maps for Pt and Ir. Light spots indicate the presence of metals in the same areas as shown by the dark spots of the zero loss image.

Table 2

Pressure effect on the activity and selectivity at 603 K.

	Pt			Ir			PtIr(SI)			PtIr(OG)		
	8	16	64	8	16	64	8	16	64	8	16	64
Pressure (kPa)	8	16	64	8	16	64	8	16	64	8	16	64
TOF	184	328	985	15	67	124	30	61	100	291	575	1257
ROP	10	77	96	2	2	27	26	68	63	34	79.5	87
Fragments	2	5.5	4	51	64	64	9	11.5	29	5	7.5	7.5
Benzene	65	14	0	35	26	6	50	16	7	44	10	5
Others ^a	23	3.5	0	12	8	3	15	4.5	1	17	3	0.5

^a Methylcyclopentene(s) plus hexenes.**Table 3**Temperature effect on the activity and selectivity at $p(\text{H}_2) = 64$ kPa.

	Pt			Ir			PtIr(SI)			PtIr(OG)		
	543	573	603	543	573	603	543	573	603	543	573	603
Temperature (K)	543	573	603	543	573	603	543	573	603	543	573	603
TOF	165	482	985	95	115	124	85.5	118	100	585	1128	1257
ROP	97	97	96	30.5	27	27	96	84	63	95	91	87
Fragments	2	2	4	60.5	66	64	3	14	29	4.5	8	7.5
Benzene	0.7	1	0	4.5	5.5	6	0.5	1.5	7	0.3	1	5
Others ^a	0.3	0	0	4	1.5	3	0.5	0.5	1	0.1	0	0.5

^a Methylcyclopentene(s) and hexenes.

ucts. Lower TOF values were characteristic of Ir with fragmentation as the main reaction, first of all, at high H_2 pressure. Adding 0.2% Ir to Pt catalyst by successive impregnation resulted, compared with the Pt parent, in a slight decrease in the activity and an increase in the fragmentation selectivity with a decrease in ROP activity. The ROP and fragmentation selectivities were closer to Pt than to monometallic Ir. When Ir was added using organometallic grafting (OG), the activity of the catalyst was highest of all samples. The ROP vs. fragment selectivities resembled to the values reported for Pt. Iridium located on the surface of Pt could cut carbonaceous deposits and thus increase the ROP activity of Pt sites. Consequently, in the case of PtIr(SI) separate Pt and Ir particles on the alumina surface could be suggested while in the case of PtIr(OG) Ir was attached to Pt, due to the organometallic grafting.

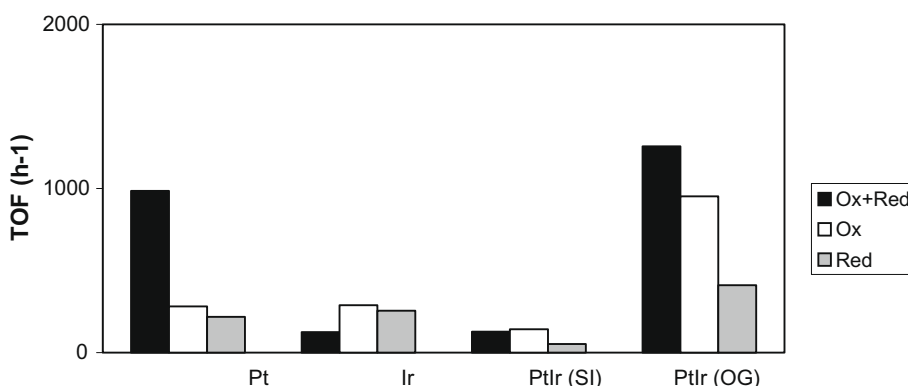
Increasing the temperature from 543 to 603 K brought about more than a fivefold increase in the TOF values over Pt (Table 3). It doubled the activity over PtIr(OG), highest again under all conditions. The temperature dependence was much smaller in the case of Ir and could even turn backwards with PtIr(SI) where the TOF at 603 K was lower than at 573 K. The tendencies of selectivities were similar as discussed above: much ROP on Pt much fragments on Ir. The bimetallic catalysts behaved somewhat differently: ROP selectivity on PtIr(OG) was nearly as high as over Pt and high also on PtIr(SI). Both PtIr samples produced less $\text{C}_1\text{--C}_5$ products than

monometallic Ir catalyst, similarly to that reported for $\text{Rh}/\text{Al}_2\text{O}_3$ vs. $\text{PtRh}/\text{Al}_2\text{O}_3$ [5,27] (Rh alone has also a high fragmentation activity [11]. Benzene formation at higher temperature was much lower (Table 2) than reported for PtRh/SiO_2 catalyst [28].

3.2.2. Effect of treatments

An oxidative treatment caused a drop of the TOF values of Pt and PtIr(OG). A reverse effect appeared on Ir and PtIr(SI). Reduction caused further dropping of the activity (Fig. 2). The quantitative effect was rather conspicuous with Pt and PtIr(OG) and not so pronounced with the (lower) activities of the other two catalysts: Ir and PtIr(SI).

As for the selectivities, oxidation decreased ROP selectivities in all four cases (Fig. 3). It was most pronounced over Ir (where almost all products were fragments after oxidation). The fragment production was more important for the PtIr(SI) catalyst than for the PtIr(OG). For PtIr(SI) catalyst, the selectivity pattern showed hardly any changes upon oxidation treatment only, but the pattern changed dramatically; hence the catalyst had only a reduction treatment: leaving benzene plus unsaturated hydrocarbons ("others") as predominant products. This phenomenon needs further studies. For the OG catalyst, there was hardly any difference in the product distribution between an oxidation treatment and a reduction treatment.

**Fig. 2.** Effect of oxidative and reductive treatments on the TOF values of MCP reactions. $T = 603$ K, $p(\text{H}_2) = 64$ kPa.

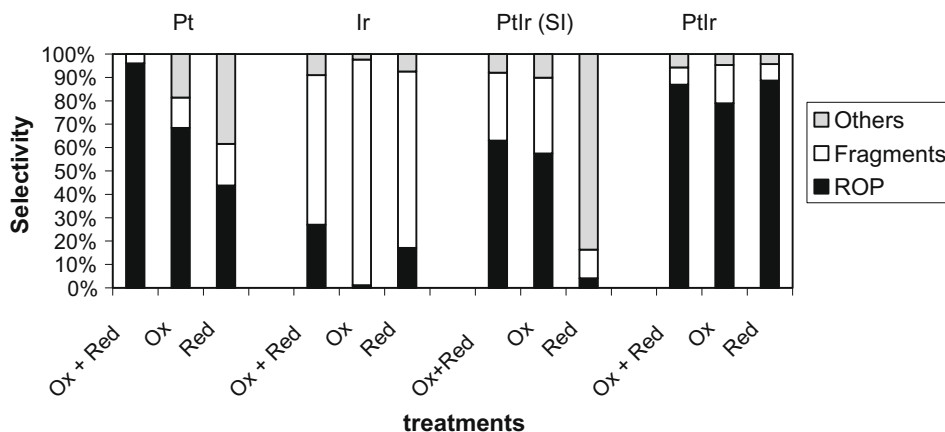


Fig. 3. Selectivities of MCP reactions after different treatments. $T = 603$ K, $p(\text{H}_2) = 64$ kPa. Benzene and hexanes are shown combined as “others”.

The difference between the two catalysts confirmed the previous hypothesis. So, we deduced that on the PtIr(SI) catalyst, Pt and Ir particles were separated on the alumina surface, and both metals could exhibit their peculiar catalytic properties. Conversely, in the case of PtIr(OG), Ir was exclusively attached to Pt, which was ensured by the organometallic grafting method. Small Ir ensembles (perhaps even single atoms) could not demonstrate their own catalytic properties, but efficiently increased the activity of Pt, maybe due to a lower carbonization caused by the enhanced C–C bond rupture activity of Ir. Its somewhat smaller ROP selectivity as opposed to Pt was, likely, due to the same reason. Ir stabilized the catalyst also against the effects of oxidation and reduction (Figs. 2 and 3).

4. Conclusions

Catalytic reaction of MCP, supported by physical characterization methods, proved to be a useful and efficient technique to obtain information on behaviors of the two bimetallic Pt–Ir/ Al_2O_3 catalyst composition, prepared by two methods. Adding Ir to Pt catalysts by successive impregnation and organometallic grafting results in catalysts with different structure: likely separate Pt and Ir sites in the former case and demonstrated bimetallic PtIr sites in the second case. These latter catalysts are more active and promising in the non-degradative ring opening reaction of MCP.

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