



Relationship between the structural properties of supported bimetallic Pt–Rh catalysts and their performances for methylcyclopentane ring opening

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ABSTRACT

Bimetallic Pt–Rh catalysts supported on alumina and silica were synthesized either by the refilling method or by coimpregnation. They were characterized by transmission electron microscopy (TEM), H₂ chemisorption, temperature-programmed reduction (TPR), Fourier transform infrared (FTIR) of adsorbed CO and the test reaction of cyclohexane dehydrogenation. Varying the preparation procedure and the nature of the support leads to the formation of bimetallic Pt–Rh particles of different size in the range 1.2–2.7 nm. A Pt surface enrichment and the presence of a Pt–Rh alloy were detected by FTIR of adsorbed CO on the largest particles.

The catalytic performances of the Pt–Rh systems were evaluated in methylcyclopentane (MCP) ring opening (RO) under pressure (28.5 bar). All the bimetallic catalysts present an activity much higher than that of the Pt monometallic sample, close to that of the Rh one. At 300 °C, the turnover frequencies are the followings: 115 h⁻¹ for Pt, 4094 h⁻¹ for Rh, between 2264 and 5563 h⁻¹ for the Pt–Rh catalysts whatever the preparation procedure and the nature of the support. On Pt–Rh samples presenting particles with large enough size (>1.7 nm), the RO selectivity at iso-conversion (>50%) is higher than those of monometallic Pt/Al₂O₃ and Rh/Al₂O₃ systems, reaching the performances of a monometallic iridium-based sample considered as the most selective catalyst in these conditions. Finally, the refilling method allows obtaining supported Pt–Rh catalysts with the structural properties required to obtain both high activity and RO selectivity during methylcyclopentane hydrogenolysis.

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1. Introduction

The selective ring opening (RO) of naphthenic molecules is a reaction of interest for the valorization of various products resulting from catalytic reforming and cracking processes [1–3]. Indeed, the hydrogenation of aromatic compounds followed by a selective opening of the obtained naphthenes to paraffins allows improving notably the fuel quality, by the selective formation of substituted paraffins in the case of gasoline or linear ones in the case of diesel. The selective ring opening reaction requires the hydrogenolysis of only one endocyclic C–C bond while avoiding the secondary reactions of deep hydrogenolysis.

In this research field, the ring opening of methylcyclopentane (MCP) is often used as a probe reaction in the investigation of the structure sensitivity of several hydrocarbon conversions catalysed by noble metal-based catalysts [4–7]. Nevertheless, in a large majority of studies, this reaction is not performed under refining conditions, i.e. under both high pressure and temperature. Most of the studied catalytic systems are composed of supported mono-

metallic noble metal-based catalysts, among which Ir-based systems lead generally to the best performances in terms of MCP conversion and selectivity to RO products [8]. Nevertheless, iridium is not available in great quantity at the natural state, making impossible the manufacture of such catalysts to industrial scale for their implementation in ring opening units. In this context, the development of bimetallic systems showing catalytic performances comparable to those of Ir catalysts presents an interesting challenge for the researchers. Several bimetallic couples are reported in the literature concerning the MCP ring opening performed at low or atmospheric pressure, as Pt/Al₂O₃ or Pt/SiO₂ systems modified by Sn, Ru, Au or Ge [9–13], Rh/Al₂O₃ or Rh/TiO₂ modified by Pd, Ge, Sn or Ag [14–17] or Ir–Au/Al₂O₃ catalysts [18]. In these studies, the bimetallic catalysts were prepared by coimpregnation, sequential impregnation, underpotential deposition or organometallic grafting. In most cases, the addition of the modifier onto the monometallic catalyst surface induces significant changes in MCP conversion and/or products distribution, in the degree of deactivation due to coke deposition or in resistance to poisoning by sulphur molecules introduced in the charge. The authors interpreted these phenomena in term of a modification of the ring opening mechanism induced by the presence of the additive in the based-metal neighbourhood.

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Recently, we have studied the catalytic performances of several bimetallic platinum-based catalysts for MCP ring opening under high pressure conditions [19]. Two types of additives were used, either inactive metals for MCP hydrogenolysis, such as copper or germanium, or active ones, such as ruthenium and rhodium. Among the studied catalysts, only Pt–Rh/Al₂O₃ samples showed both activity and RO selectivity higher than those of monometallic Pt/Al₂O₃ and Rh/Al₂O₃ systems, reaching the performances of an iridium-based sample tested in the same conditions. In this previous work, the Pt–Rh/Al₂O₃ catalysts were prepared by a surface redox reaction (namely the refilling method) that consists of depositing the rhodium additive by reduction of its precursor salt by hydrogen preadsorbed on the platinum surface. However, the characterization of the synthesized Pt–Rh/Al₂O₃ catalysts was not exposed in the previous paper [19] and the arrangement of platinum and rhodium atoms at the support surface was not determined. Consequently, at the end of this previous study, we were not able to conclude whether the particular behaviour of this bimetallic system was directly linked to its particular preparation method.

The present study will try to highlight the various parameters that can modulate the catalytic performances for MCP RO of the supported bimetallic Pt–Rh systems by varying their preparation methods and the support. The classical preparation method by coimpregnation was used in parallel with the refilling method, as well as two oxides (alumina and silica) for the support. The bimetallic catalysts were characterized by H₂ chemisorption and transmission electron microscopy (TEM), by temperature-programmed reduction, by Fourier transform infrared spectroscopy of adsorbed CO and by the test reaction of cyclohexane dehydrogenation. Our aim was to characterize in depth the bimetallic Pt–Rh samples in order to explain the relationship between their structure and their catalytic performances for the RO reaction of methylcyclopentane under pressure.

2. Experimental

2.1. Catalyst preparation

The supports were γ -alumina (from AXENS) and silica (from DEGUSSA) with specific surface areas (S_{BET}) of 215 and 175 m² g⁻¹, respectively. The supports were crushed and sieved, in order to retain particles with sizes between 0.25 and 0.40 mm, and calcined in flowing air at 450 °C for 4 h.

The monometallic 0.6 wt%Pt/Al₂O₃, 0.6 wt%Rh/Al₂O₃ and 0.6 wt%Ir/Al₂O₃ catalysts were prepared by impregnation of the precursor salts (H₂PtCl₆, RhCl₃, H₂IrCl₆) in an HCl solution (pH = 1). After evaporation of the solvent, the catalyst was activated by calcination at 450 °C (Pt/Al₂O₃) or 300 °C (Rh/Al₂O₃ and Ir/Al₂O₃) under air (4 h) and reduced under hydrogen at 500 °C (4 h). Rh/Al₂O₃ and Ir/Al₂O₃ catalysts were characterized in [19]. Briefly, they contain 1 wt% and 1.2 wt% of chlorine and their dispersions are 56% and 85%, respectively.

Bimetallic Pt–Rh/Al₂O₃ catalysts were prepared either by surface redox reaction or by coimpregnation using each time RhCl₃ as Rh precursor salt. In the case of SiO₂ support, only the coimpregnation method was retained. The deposition of the Rh modifier of the monometallic Pt/Al₂O₃ catalyst (called “parent” catalyst) by surface redox reaction was performed according to the “refilling method” described elsewhere [19]. In this study, the solution containing the RhCl₃ modifier salt in hydrochloric acid medium (pH = 1) was let in contact with the parent catalyst under nitrogen flow for 5 min. Finally, the solution was filtered out after reaction and the catalyst was dried overnight before to be reduced under hydrogen flow at 500 °C for 1 h (2 °C min⁻¹ heating rate). The Rh

content deposited on the catalyst by the refilling method was determined by ICP-OES spectroscopy. For the coimpregnation method, the H₂PtCl₆ and RhCl₃ salts were simultaneously added to the alumina support maintained at pH = 1 by HCl addition or directly to the silica support. The solution was gently stirred for 1 h at room temperature. Then, the slurry was dried on a sand bath until the solid was visibly dry. Drying was completed in an oven at 120 °C overnight. The catalyst was finally conditioned by heating in air at 300 °C for 4 h, flushing with nitrogen and then reducing in hydrogen (60 mL min⁻¹) at 500 °C for 4 h. Heating ramps were programmed at 10 °C min⁻¹.

The chlorine content on each catalyst was determined at the “Service central d’analyse” of the CNRS.

2.2. Transmission electron microscopy (TEM) measurements

TEM measurements were performed on a JEOL 2100 electron microscope operating at 200 kV with a LaB₆ source and equipped with a Gatan Ultra scan camera. All the samples were embedded in a polymeric resin (spur) and cut into a section as small as 40 nm with an ultramicrotome equipped with a diamond knife. Cuts were then deposited on an Al grid previously covered with a thin layer of carbon. Average particle sizes were determined by measuring at least 100 particles for each sample analysed, from at least five different micrographs. Microanalysis of Pt and Rh was carried out by energy dispersive X-ray spectroscopy (EDX) in the nanoprobe mode.

2.3. Hydrogen chemisorption

The metallic accessibility or dispersion ($D\%$) was determined from H₂ chemisorption measurement, carried out in a pulse chromatographic system, using a stoichiometry H/Metal equal to one. It is known [20] that this may lead to erroneous relative metallic dispersions but we have checked that the values of the particle size estimated by the hydrogen chemisorption measurements are in accordance with those determined from the TEM pictures.

2.4. Temperature-programmed reduction (TPR) experiments

The TPR experiments were performed with a 1.0vol% H₂/Ar gas mixture. The sample was heated in the temperature range of 25–500 °C with a ramp of 5 °C min⁻¹ and then maintained at 500 °C for 1 h. The hydrogen uptake was monitored by a thermal conductivity detector. Prior to the TPR, the catalysts were first pretreated *in situ* under oxygen for 30 min at 300 °C and cooled down to room temperature.

2.5. Fourier transform infrared (FTIR) spectroscopy study of adsorbed CO

Transmission FTIR spectra were collected in the single-beam mode, with a resolution of 2 cm⁻¹, using a Nicolet Nexus FTIR spectrometer. Catalyst samples were prepared as self-supported wafers with a diameter of 12 mm and a “thickness” of approximately 20 mg cm⁻².

Prior to CO adsorption experiments, all the catalysts were reduced *in situ* for 1 h under H₂ at 500 °C, then outgassed at this temperature before to be cooled to room temperature. Reference spectra of the clean surfaces were collected at room temperature. CO was introduced to the cell, which was then purged to remove any weakly bonded CO. Spectra were collected until steady state was reached. Difference spectra between the samples and the corresponding reference are shown in this paper. Spectral deconvolution was performed using the Galactic PeakSolve peak-fitting program. All deconvoluted spectra shown in this paper are

converged solutions, with correlation factors above 0.999 and standard errors below 0.004.

2.6. Cyclohexane dehydrogenation

The test reaction of cyclohexane dehydrogenation to benzene was performed in order to study the effect of the Rh deposit on the Pt metallic phase. This reaction was carried out in a continuous flow reactor at 270 °C under atmospheric pressure on 10 mg of catalyst. The detailed protocol was described elsewhere [19].

2.7. Ring opening of methylcyclopentane (MCP)

MCP hydrogenolysis was performed under a total pressure of 28.5 bar with a molar ratio $\frac{H_2}{MCP} = 7.5$ in a temperature range from 200 to 425 °C according to the experimental protocol described elsewhere [19]. The absence of diffusion limitations in these experimental conditions was checked by varying independently the particle size (in the 0.1–0.6 mm range), the amount of catalyst (from 125 mg to 500 mg) and the reactant flow rates (from 0.0334 to 0.1336 mL min⁻¹). Conversion, defined as the percentage of MCP converted, was determined as a function of temperature. The only reaction products were 2-methylpentane, 3-methylpentane, *n*-hexane and C1–C5 products. Neither cyclohexane nor benzene was detected as reaction products. The selectivity of the catalysts for ring opening (hydrogenolysis of only one endocyclic C–C bond) was estimated from the yield in C1–C5 products resulting from deep hydrogenolysis: the lowest the C1–C5 yield, the highest the RO products yield and then the highest the MCP ring opening selectivity. The yield of C1–C5, defined as the percentage of MCP converted into C1–C5 products, was reported as a function of the conversion. It was verified that the yield in C1–C5 obtained for a given conversion is independent of the reaction conditions by varying the WHSV instead of the temperature. For all the catalysts, the “Conversion = f(Temperature)” and “C1–C5 yield = f(Conversion)” curves will be always studied simultaneously in order to compare their catalytic performances since the effects of temperature and conversion are linked in our experimental conditions.

3. Results and discussion

3.1. Main characteristics of the supported Pt–Rh catalysts

3.1.1. Preparation of the Pt–Rh catalysts by MR and CI methods

Table 1 displays the main characteristics of the various bimetallic Pt–Rh catalysts supported on either alumina or silica and prepared either by surface redox reaction (refilling method labelled

“RM”) or by classical coimpregnation (labelled “CI”). The refilling method was used to synthesize a series of bimetallic 0.6 wt%Pt–*x* wt%Rh/Al₂O₃ catalysts by modifying a monometallic 0.6 wt%Pt/Al₂O₃ catalyst (“parent” catalyst) with several successive refillings of 0.2 wt%Rh. Table 1 shows that the Rh content really deposited on the catalyst increases logically with the theoretical wt%Rh introduced in solution, but the Rh deposit is not total. However, for a same Rh content introduced in solution, the present RM method allows depositing more important Rh quantities on platinum than the redox method used in our previous study [19], i.e. a refilling step followed by a catalytic reduction step under hydrogen (deposit of 0.46 wt% vs. 0.17 wt%Rh, respectively, for 0.80 wt%Rh introduced in solution). Coimpregnated 0.6 wt%Pt–0.3 wt%Rh catalysts were also prepared on alumina and silica, the chosen Rh content being in the middle of the range of the RM samples series.

In Table 1, the characteristics of the Pt–Rh/Al₂O₃–RM catalysts are compared to those of both monometallic Pt/Al₂O₃ catalysts named “parent” and “blank”, respectively. To prepare the blank Pt/Al₂O₃ sample, the parent catalyst was treated under hydrogen in a HCl solution of pH = 1. This treatment corresponds to the preparation protocol of the RM bimetallic catalysts, but without addition of the Rh precursor salt. The blank treatment influences somewhat the characteristics of the parent Pt/Al₂O₃ catalyst. Besides a slight increase of the chlorine content, an increase of the metal particles size is noticed. This sintering phenomenon induced by the actual preparation procedure by surface redox reaction was already observed on various monometallic and bimetallic catalysts under similar conditions [21,22]. Thus, this phenomenon can explain the low metallic accessibility value of the bimetallic 0.6 wt%Pt–0.36 wt%Rh/Al₂O₃–RM catalyst compared to that of the 0.6 wt%Pt–0.3 wt%Rh/Al₂O₃–CI sample (0.36 vs. 0.77). On the other hand, the CI catalyst supported on silica presents a metallic accessibility comparable with that of Pt–Rh/Al₂O₃–RM system (0.41 vs. 0.36) and thus much lower than that of the CI catalyst supported on alumina. This result is not surprising since it is known that on silica the metal–support interactions are rather weak compared to alumina. Moreover, silica support retains less chlorine, since the chlorine content measured on the Pt–Rh/SiO₂–CI sample is three to four times lower than that of the Pt–Rh/Al₂O₃ catalysts.

Fig. 1 shows representative TEM images, as well as the corresponding particle size distributions for the three bimetallic Pt–Rh catalysts with Rh content close to 0.3 wt%. The average particle sizes of all the samples examined by TEM are reported in Table 1. A good homogeneity is highlighted on TEM pictures with the presence of small metal particles well distributed on the alumina or silica support. As observed previously by H₂ chemisorption, Fig. 1b and c shows that the average particle size of Pt–Rh catalysts prepared by CI method is notably different according to the sup-

Table 1

Characteristics of the supported 0.6 wt%Pt–*x* wt%Rh catalysts prepared by refilling method (RM) or by coimpregnation (CI), compared with those of monometallic parent and blank 0.6 wt%Pt/Al₂O₃ samples.

Catalyst	wt%Rh theoretical	wt%Rh deposited	wt%Cl	H/M ^a	<i>d</i> (nm) ^b	<i>d</i> (nm) ^c
Pt/Al ₂ O ₃ –parent	–	–	1.36	0.75	1.3	<i>n.d.</i>
Pt/Al ₂ O ₃ –blank	–	–	1.54	0.55	1.7	<i>n.d.</i>
Pt–Rh/Al ₂ O ₃ –RM	0.20	0.11	1.25	<i>n.d.</i>	<i>n.d.</i>	2.3
	0.40	0.23	1.40	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
	0.60	0.36	1.40	0.36	2.6	2.4
	0.80	0.46	1.30	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
	2.00	0.85	1.50	<i>n.d.</i>	<i>n.d.</i>	2.7
Pt–Rh/Al ₂ O ₃ –CI	0.30	0.30	1.70	0.77	1.2	1.2
Pt–Rh/SiO ₂ –CI	0.30	0.30	0.45	0.41	2.3	2.4

n.d.: not determined.

^a Determined from H₂ chemisorption.

^b Deduced from H/M value.

^c Deduced from TEM analysis.

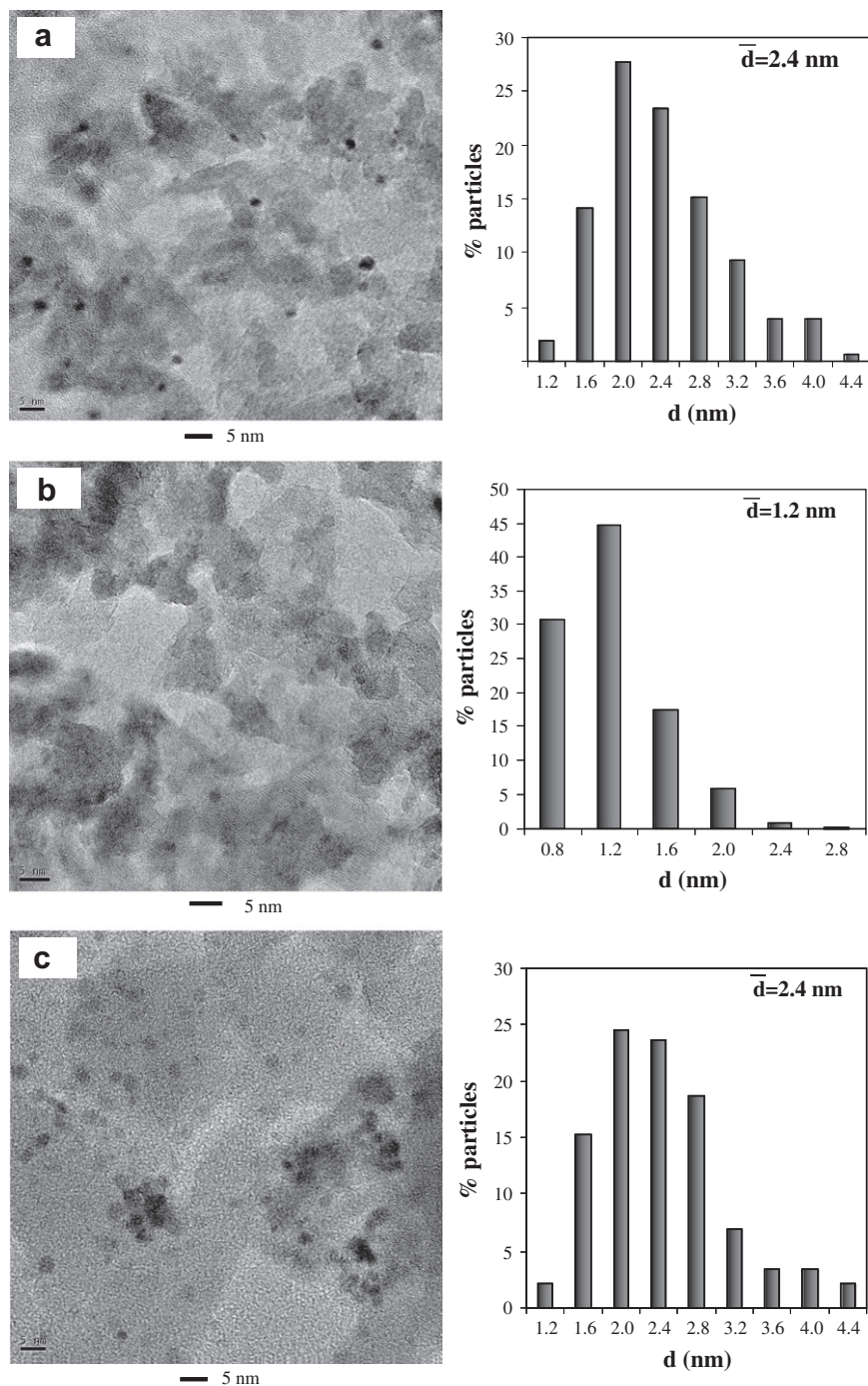


Fig. 1. TEM images and particle size distributions of: (a) Pt-0.36Rh/Al₂O₃-RM; (b) Pt-0.30Rh/Al₂O₃-CI; (c) Pt-0.30Rh/SiO₂-CI.

port nature: 2.4 nm for Pt-Rh/SiO₂-CI sample against 1.2 nm for Pt-Rh/Al₂O₃-CI system. Finally, whatever the studied sample, the average particle sizes deduced from TEM analysis and chemisorption measurements are in perfect agreement (Table 1). Concerning the RM samples, a slight enlargement of the metal particles is observed with the quantity of deposited Rh from 2.3 nm (0.11 wt%Rh) to 2.7 nm (0.85 wt%Rh). EDX analysis of metal crystallites reveals the presence of platinum and rhodium in the same particle on all the Pt-Rh systems. Moreover, for the RM catalysts, the Rh quantity within a metal particle increases with the deposited Rh content, which allows explaining the enlargement phenomenon observed previously by TEM.

3.1.2. Sintering treatments of the Pt-Rh/Al₂O₃-CI catalyst

The previous results indicated that for similar metallic compositions, the supported Pt-Rh catalysts displayed average particle sizes strongly influenced by the preparation procedure and the support used. Thus, on the alumina support, both RM and CI preparation methods does not lead to bimetallic Pt-Rh/Al₂O₃ catalysts of comparable particle sizes. In order to compare latter equitably the catalytic performances for MCP hydrogenolysis of both samples, the CI catalyst was submitted to various treatments in order to enlarge its metal particles. The first one consisted to subject the Pt-Rh/Al₂O₃-CI sample to a blank treatment, i.e. a treatment under hydrogen flow in HCl solution of pH = 1. The second one

consisted in activating Pt–Rh/Al₂O₃–Cl system under nitrogen flow and steam at 400 °C during 2 h.

The main characteristics of the bimetallic catalysts treated in such ways (named Pt–Rh/Al₂O₃–Cl–HCl and Pt–Rh/Al₂O₃–Cl–T, respectively) are given in Table 2. Both treatments undergone by Pt–Rh/Al₂O₃–Cl catalyst involve a slight decrease in the chlorine content and above all a decrease in metal accessibility values, especially for the blank treatment (Pt–Rh/Al₂O₃–Cl–HCl catalyst). Nevertheless, these values remain higher than those observed for Pt–Rh/Al₂O₃–RM and Pt–Rh/SiO₂–Cl catalysts. A good agreement is obtained between the average particle sizes measured by TEM and the metal accessibility values determined by H₂ chemisorption. Moreover, on these catalysts, the presence of platinum and rhodium within the same metal particle is still highlighted by EDX analysis, i.e. none of the treatments induced segregation of the two metals.

3.2. Characterization of the metallic function of the supported Pt–Rh catalysts

3.2.1. Activity for the cyclohexane dehydrogenation

Cyclohexane dehydrogenation towards benzene performed under atmospheric pressure is a reaction catalysed by the metal function and considered generally as structure insensitive [23]. Therefore, the activity is directly proportional to the number of surface active atoms [24,25]. The relative activities obtained on all the supported bimetallic Pt–Rh catalysts reported to that of the corresponding monometallic sample (i.e. either the Pt/Al₂O₃–blank system for the RM series or the Pt parent system supported on Al₂O₃ or SiO₂ for the CI catalysts) are plotted in function of the deposited Rh content in Fig. 2. For comparison, the relative activity of a 0.6 wt%Rh/Al₂O₃ catalyst is presented on the same figure.

First, it should be noticed that, whatever the preparation method (MR, CI, CI + sintering treatment) and the support used, the addition of rhodium inhibits the platinum activity. Concerning the bimetallic Pt–Rh/Al₂O₃–RM catalysts, Fig. 2 shows that the inhibiting effect increases with the quantity of deposited rhodium. This inhibiting effect indicates the existence of an interaction between rhodium and platinum, rhodium being less active than platinum for this reaction. However, the bimetallic interaction or more exactly the nature of the active surface of the Pt–Rh systems seems to depend on the preparation method and the support. Thus, for a same content of deposited Rh (approximately 0.3 wt%), the relative activities for cyclohexane dehydrogenation of the supported Pt–Rh samples are quite comparable except in the case of the Pt–Rh/Al₂O₃–Cl system that is less active than all the others. As this last system possesses the highest metal accessibility among the various bimetallic catalysts (Table 1), its lowest relative activity could be explained by a larger amount of rhodium on the bimetallic Pt–Rh particle surface. After undergoing sintering treatments (in HCl medium or by thermal activation), the relative activity of the Pt–0.30Rh/Al₂O₃–Cl catalyst reaches values comparable to those of

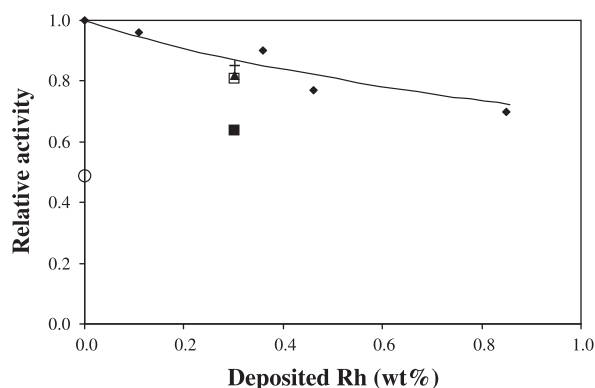


Fig. 2. Relative activity for cyclohexane dehydrogenation of supported bimetallic Pt–Rh catalysts: (◆) Pt–Rh/Al₂O₃–RM (reported to Pt/Al₂O₃–blank sample); (■) Pt–Rh/Al₂O₃–Cl, (+) Pt–Rh/Al₂O₃–Cl–HCl and (▲) Pt–Rh/Al₂O₃–Cl–T (reported to Pt/Al₂O₃–parent sample); (□) Pt–Rh/SiO₂–Cl (reported to a Pt/SiO₂ sample); (○) 0.6 wt%Rh/Al₂O₃ catalyst (reported to Pt/Al₂O₃–parent sample).

its counterparts of same average particle size but prepared by RM method or on silica support. These results would mean that the more the bimetallic Pt–Rh particles are large, the less their surface is rich in rhodium.

To conclude this part, cyclohexane dehydrogenation seems to indicate that small Pt–Rh particles have more rhodium atoms at their surface than the largest ones, for the same platinum and rhodium content. Then, it can be inferred on a platinum enrichment on large Pt–Rh particles.

3.2.2. Characterization by temperature-programmed reduction

The reduction in the catalysts pre-oxidized at 300 °C was followed by the temperature-programmed reduction technique. Fig. 3A shows the TPR profiles of two bimetallic Pt–Rh/Al₂O₃–RM catalysts (with 0.11 and 0.36 wt%Rh, respectively) compared to the profiles of monometallic 0.6 wt%Pt/Al₂O₃ (parent and blank) and 0.3 wt%Rh/Al₂O₃ samples. The Pt/Al₂O₃–parent and Pt/Al₂O₃–blank catalysts present a reduction peak with maxima located at 236 °C and 214 °C, respectively (Fig. 3A, profiles a and b). This shift to a lower temperature can be explained by the increase of the metal particle size of the parent catalyst after the blank treatment, inducing a weaker metal–support interaction on the blank catalyst [22]. The reduction curves of the bimetallic RM catalysts are quite comparable with two peaks centred, respectively, at 95 °C and 258 °C (Fig. 3A, profiles c and d). Moreover, the surface of the peak at lower temperature increases with the rhodium content. Finally, the TPR profile of the monometallic Rh catalyst presents one reduction peak between 50 and 250 °C, with a maximum at 130 °C (Fig. 3A, profile e).

The hydrogen consumptions deduced from TPR curves are reported in Table 3. For the monometallic Pt and Rh catalysts, the values of H₂/M ratios indicate that, after calcination at 300 °C, platinum and rhodium were almost completely oxidized in the PtO₂ (theoretical H/M = 2) and Rh₂O₃ (theoretical H/M = 1.5) forms, respectively. The addition of rhodium to platinum by the RM technique contributes to increase the hydrogen consumption compared to the monometallic Pt catalysts, leading to H₂/M ratios intermediate between those of the Rh/Al₂O₃ and Pt/Al₂O₃–blank systems. The quantities of consumed hydrogen by the bimetallic RM catalysts correspond approximately to those necessary to reduce the monometallic 0.6 wt%Pt/Al₂O₃–blank and 0.3 wt%Rh/Al₂O₃ systems, by taking into account the Pt and Rh contents in these bimetallic samples. Nevertheless, according to Table 3, it is clear that the first peak of hydrogen consumption observed on the Pt–Rh/Al₂O₃–RM catalysts does not correspond only to the

Table 2

Characteristics of the 0.6 wt%Pt–0.30 wt%Rh/Al₂O₃ catalysts prepared by coimpregnation (CI) and submitted to various sintering treatments.

Catalyst	Sintering treatment	wt%Cl	H/M ^a	<i>d</i> (nm) ^b	<i>d</i> (nm) ^c
Pt–Rh/Al ₂ O ₃ –Cl	–	1.70	0.77	1.2	1.2
Pt–Rh/Al ₂ O ₃ –Cl–HCl	HCl (pH = 1)/H ₂	1.51	0.50	1.8	1.7
Pt–Rh/Al ₂ O ₃ –Cl–T	H ₂ O/N ₂ /400 °C	1.43	0.60	1.6	1.5

^a Determined from H₂ chemisorption.

^b Deduced from H/M value.

^c Deduced from TEM analysis.

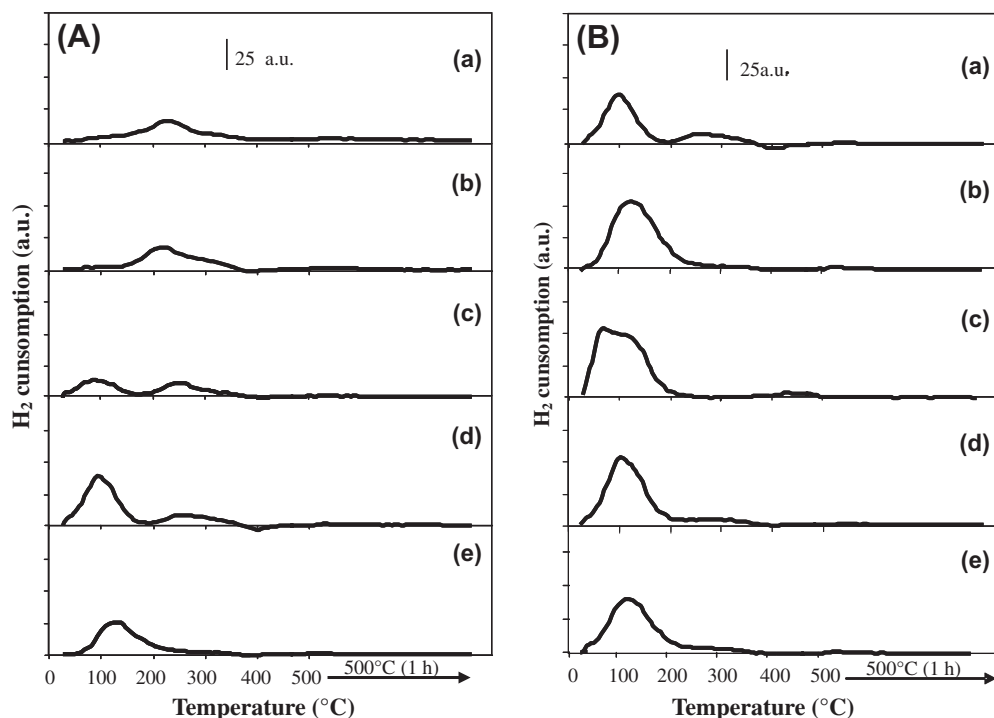


Fig. 3. (A) TPR profiles of Pt–Rh/Al₂O₃–RM catalysts compared with the Pt/Al₂O₃ and Rh/Al₂O₃ ones: (a) Pt/Al₂O₃–parent, (b) Pt/Al₂O₃–blank, (c) Pt–0.11 wt%Rh/Al₂O₃, (d) Pt–0.36 wt%Rh/Al₂O₃ and (e) 0.3 wt%Rh/Al₂O₃. (B) TPR profiles of Pt–Rh catalysts (containing around 0.30 wt%Rh) prepared by different methods: (a) Pt–0.36 wt%Rh/Al₂O₃–RM, (b) Pt–0.30 wt%Rh/Al₂O₃–CI, (c) Pt–0.30 wt%Rh/SiO₂–CI, (d) Pt–0.30 wt%Rh/Al₂O₃–CI–HCl and (e) Pt–0.30 wt%Rh/Al₂O₃–CI–T.

Table 3

Hydrogen consumptions during TPR analysis of the supported 0.6 wt%Pt–*x* wt%Rh catalysts prepared by refilling method (RM) or by coimpregnation (CI), compared with those of monometallic 0.6 wt%Pt/Al₂O₃ (parent and blank) and 0.3 wt%Rh/Al₂O₃ samples.

Catalyst	<i>T</i> _{max} (°C)	H ₂ consumed (μmol g _{cat} ^{−1})	Total number of metal atoms (μmol g _{cat} ^{−1})	H ₂ /M
Pt/Al ₂ O ₃ –parent	236	60	31	1.9
Pt/Al ₂ O ₃ –blank	214	55	31	1.8
Pt–0.11Rh/Al ₂ O ₃ –RM	95	45	42	1.6
	258	24		
Pt–0.36Rh/Al ₂ O ₃ –RM	95	74	66	1.5
	258	25		
Pt–0.30Rh/Al ₂ O ₃ –CI	130	83	60	1.4
Pt–0.30Rh/SiO ₂ –CI	58, 116	78	60	1.3
Pt–0.30Rh/Al ₂ O ₃ –CI–HCl	102, 287	73	60	1.2
Pt–0.30Rh/Al ₂ O ₃ –CI–T	124, 287	69	60	1.1
Rh/Al ₂ O ₃	130	43	29	1.5

reduction of Rh species, but to the reduction of bimetallic Pt–Rh entities. The second peak of consumption at higher temperature could then be assigned to the presence of small platinum particles in strong interaction with the support and/or of bimetallic Pt–Rh particles highly enriched in Pt.

Fig. 3B compares the TPR curves of supported bimetallic Pt–Rh catalysts of similar Rh content (near 0.30 wt%Rh) but prepared by different methods (RM or CI) on alumina or silica support. The TPR profiles vary notably according to the preparation method and the treatment undergone by the bimetallic samples. Indeed, on alumina support, the CI catalyst (not modified by treatment after its preparation) presents a TPR profile quite similar to that of monometallic rhodium sample, with only one reduction peak with a maximum at 130 °C (Fig. 3B, profile b). Therefore, this TPR profile is different from that of the RM system of same metallic compositions as described previously (Fig. 3A profile d and

Fig. 3B profile a). Nevertheless, as observed for RM sample, the presence of rhodium introduced by CI method contributes to increase the quantity of consumed H₂ compared to the catalyst 0.6Pt/Al₂O₃ (Table 3). On bimetallic Pt–Rh/Al₂O₃–CI catalyst presenting rather small metallic particles, the presence of only one reduction peak corresponding to such a H₂ consumption can be attributed to the reduction of bimetallic entities, inside of which rhodium catalyses the reduction of platinum.

The CI catalyst supported on silica (Fig. 3B, profile c) presents a particular curve with two reduction maxima at low temperature (58 and 116 °C). For both Pt–Rh/Al₂O₃–CI–HCl and Pt–Rh/Al₂O₃–CI–T catalysts (Fig. 3B, profiles d and e), TPR profiles are comparable to that of the Pt–Rh/Al₂O₃–RM catalyst previously observed, with two reduction peaks: a first major peak located at low temperature (102 °C and 124 °C respectively) and a second minor one at 287 °C. Finally, bimetallic Pt–Rh catalysts of comparable particle size (Pt–Rh/Al₂O₃–RM, Pt–Rh/SiO₂–CI, Pt–Rh/Al₂O₃–CI–HCl and Pt–Rh/Al₂O₃–CI–T) tend to present comparable behaviours during TPR analysis, and these results being in agreement with the tendencies observed during cyclohexane dehydrogenation.

In conclusion, the TPR characterization highlights an interaction between platinum and rhodium for all the bimetallic Pt–Rh catalysts, whatever the preparation method (RM or CI) or the support used (alumina or silica). However, this technique shows that the nature of the Pt–Rh phases differs according to the average particles size of the bimetallic sample, the size being modulated by both the preparation procedure and the nature of the support.

3.2.3. Characterization by FTIR of adsorbed CO

FTIR spectra of CO adsorbed at room temperature on supported bimetallic Pt–Rh catalysts are given in Fig. 4 compared to those of monometallic Pt and Rh catalysts.

All spectra, except spectrum d of Fig. 4B corresponding to the only catalyst supported on silica, show the existence of a band

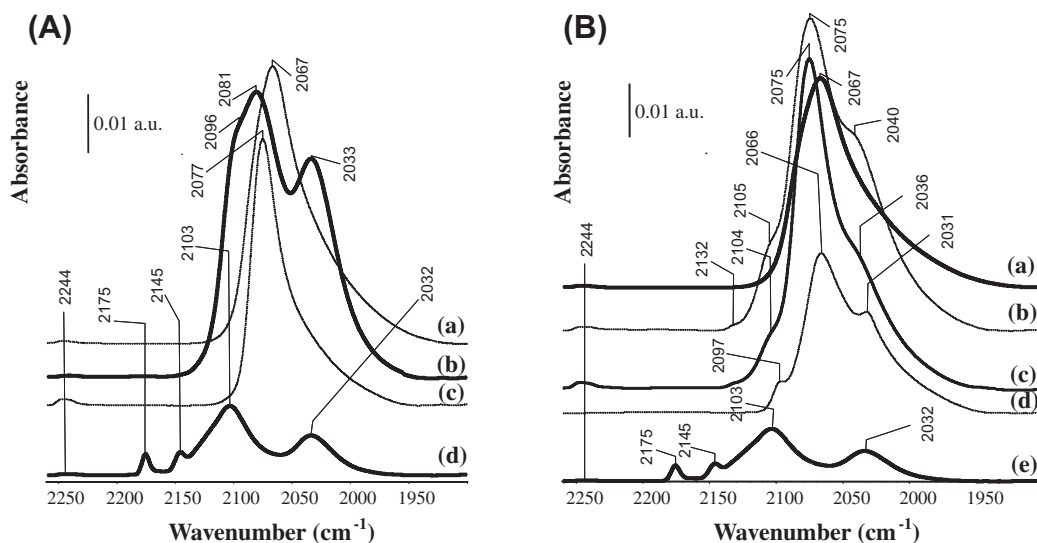


Fig. 4. (A) FTIR spectra of adsorbed CO of Pt–Rh/Al₂O₃ catalysts compared with the Pt/Al₂O₃ and Rh/Al₂O₃ ones: (a) Pt/Al₂O₃-parent, (b) Pt–0.30 wt%Rh/Al₂O₃-CI, (c) Pt–0.36 wt%Rh/Al₂O₃-RM and (d) 0.3 wt%Rh/Al₂O₃. (B) FTIR spectra of adsorbed CO of supported Pt–Rh catalysts prepared by CI method compared with the Pt/Al₂O₃ and Rh/Al₂O₃ ones: (a) Pt/Al₂O₃-parent, (b) Pt–0.30 wt%Rh/Al₂O₃-CI-T, (c) Pt–0.30 wt%Rh/Al₂O₃-CI-HCl, (d) Pt–0.30 wt%Rh/SiO₂-CI and (e) 0.3 wt%Rh/Al₂O₃.

more or less marked at 2244 cm⁻¹, attributed to CO adsorbed on the Lewis acid sites of the alumina support [26].

On the monometallic Pt/Al₂O₃ catalyst (Fig. 4A, spectrum a), FTIR analysis reveals only one intense band located at 2067 cm⁻¹ characteristic of CO adsorbed in a linear mode onto platinum (Pt⁰-CO species) [27,28]. On the monometallic Rh/Al₂O₃ catalyst (Fig. 4A, spectrum d), four distinct bands are observed: two intense ones at 2103 and 2032 cm⁻¹ and two lower ones at higher wavenumber (2145 and 2175 cm⁻¹). Similar results concerning the adsorption of CO on Rh are reported in the literature, making it possible to assign these bands in the following way [29–36]: (i) bands at 2032 and 2103 cm⁻¹ correspond to the vibrations of the gem-dicarbonyl Rh¹⁺-(CO)₂ species (antisymmetric and symmetric mode, respectively), (ii) bands at 2145 and 2175 cm⁻¹ are attributed to CO adsorbed onto Rh²⁺ and Rh³⁺ species, respectively. The presence of Rh⁺ species is generally explained by Rh oxidation in presence of CO involving hydroxyl groups of the support, according to the following reaction [37]: 2Rh + 4CO + 2AlOH → H₂ + 2Al–O–Rh(CO)₂. This phenomenon results from the higher Rh–CO binding energy than that of Rh–Rh bond (185 kJ mol⁻¹ vs. 44.5 kJ mol⁻¹). The presence of Rh²⁺ and Rh³⁺ species on catalyst pre-reduced under H₂ during 1 h at 500 °C can be surprising. However, after decomposition of the spectra into elementary bands, their relative surfaces are very weak (Fig. 5a and Table 4: 2.2% for Rh³⁺ and 1.9% for Rh²⁺), the gem-dicarbonyl species being predominant on this sample (relative surface close to 96%). The presence of Rh³⁺ oxidized species was already observed by Kondarides et al. [38] on Rh catalysts supported on CeO₂ and was attributed to the proximity of chlorine atoms that stabilize rhodium in the Rh³⁺ oxidation state. In addition, no band at 2060 cm⁻¹ corresponding to the CO linearly adsorbed (Rh⁰-CO) was observed.

The bimetallic Pt–Rh systems present different spectra according to the preparation method. The IR spectrum of adsorbed CO on the Pt–Rh/Al₂O₃-CI catalyst (Fig. 4A, spectrum b) is composed of three distinct main bands at 2096, 2081 and 2033 cm⁻¹, and these vibration frequencies are corresponding after decomposition to those observed on both monometallic platinum and rhodium catalysts spectra (Fig. 5b, Table 4). However, on this sample, the relative surface corresponding to symmetric gem-dicarbonyl species becomes very low whereas that of the antisymmetric mode is higher than that obtained for the Rh/Al₂O₃ system (51.5% vs. 33.3%, respectively). On the bimetallic Pt–0.36Rh/Al₂O₃-RM cata-

lyst (Fig. 4A, spectrum c), a main dissymmetric band is located at 2077 cm⁻¹, which can be decomposed into three main elementary peaks (Fig. 5c). The decomposition of this spectrum highlights the presence of a peak at 2061 cm⁻¹ not observed on the CI system (Table 4). Fig. 4B shows that the spectra of the Pt–0.30Rh/Al₂O₃-CI-T, Pt–0.30Rh/Al₂O₃-CI-HCl and Pt–0.30Rh/SiO₂-CI catalysts present a profile comparable to that of the Pt–0.36Rh/Al₂O₃-RM catalyst, with a main band in the 2066–2075 cm⁻¹ range and two shoulders around 2033 cm⁻¹ and 2100 cm⁻¹. Moreover, one band of very low intensity located at 2132 cm⁻¹ is observed on Pt–0.30Rh/Al₂O₃-CI-T and Pt–0.30Rh/Al₂O₃-CI-HCl catalysts, indicating the presence of Rh²⁺ species. After decomposition (example given in Fig. 5d for Pt–0.30Rh/Al₂O₃-CI-HCl sample), a band at 2059 cm⁻¹ is once again observed as on the Pt–0.36Rh/Al₂O₃-RM catalyst. Lévy et al. [39] studied the surface of monometallic catalysts containing platinum and rhodium, as well as bimetallic platinum–rhodium catalysts supported on alumina, by successive adsorptions of NO and CO followed by IR. On the bimetallic systems, these authors also observed the appearance of a band around 2060 cm⁻¹, which they attributed to a Pt–Rh alloy. Finally, in the present work, this band is only observed on the supported bimetallic Pt–Rh catalysts presenting the largest particles size, i.e. all the samples except CI catalyst deposited on alumina without subsequent sintering treatment.

In conclusion, the FTIR analysis highlights the existence of metal phases of different nature between the various Pt–Rh systems, as previously observed for the probe reaction of cyclohexane dehydrogenation and by temperature-programmed reduction. The metal phase nature of the Pt–Rh catalysts seems to be directly correlated to their particles size, with the formation of particular Pt–Rh species when the particles are large enough.

3.3. Performances of the supported Pt–Rh catalysts during MCP ring opening (RO)

3.3.1. Bimetallic Pt–Rh/Al₂O₃ catalysts prepared by refilling method (RM)

The MCP conversions as function of temperature and yields in C1–C5 products as function of MCP conversion obtained on the bimetallic Pt–Rh/Al₂O₃-RM, and monometallic 0.6Pt/Al₂O₃ (parent and blank) and 0.6Rh/Al₂O₃ catalysts are presented in Fig. 6. The catalytic performances of a 0.6 wt%Ir/Al₂O₃ catalyst are also pre-

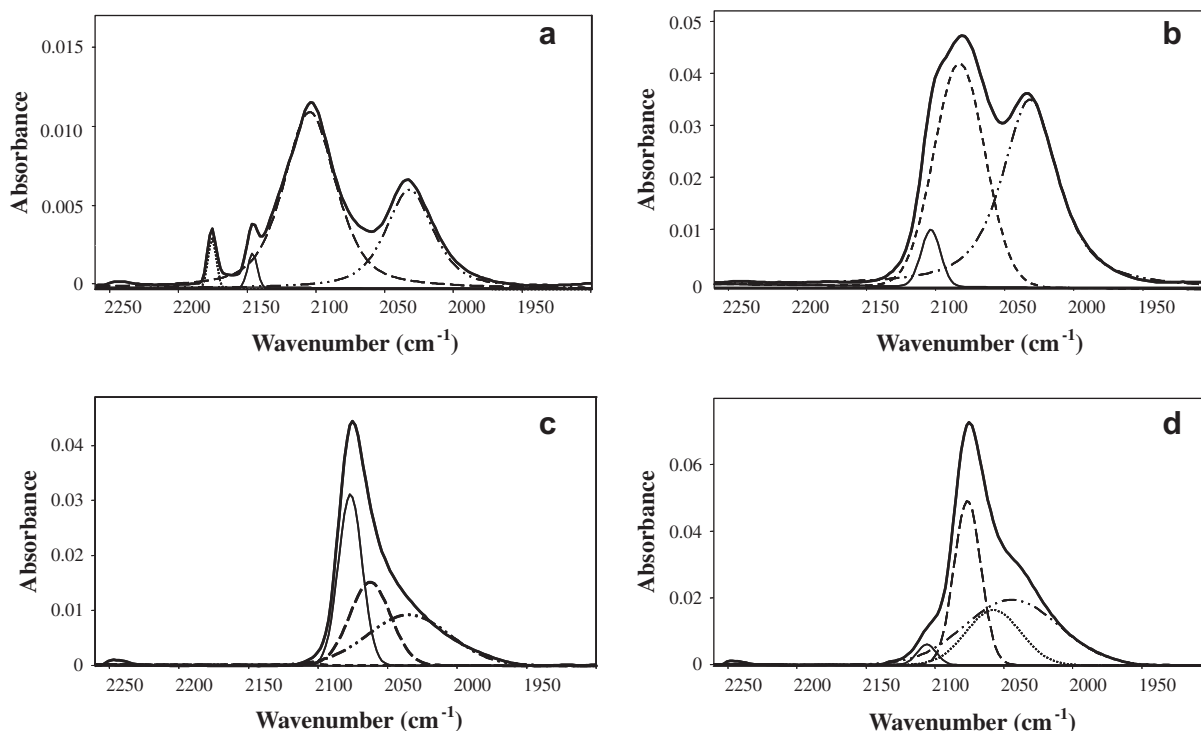


Fig. 5. FTIR spectra of adsorbed CO decomposed in elementary bands for monometallic Rh and bimetallic Pt–Rh catalysts: (a) 0.3 wt%Rh/Al₂O₃, (b) Pt–0.30 wt%Rh/Al₂O₃-Cl, (c) Pt–0.36 wt%Rh/Al₂O₃-RM and (d) Pt–0.30 wt%Rh/Al₂O₃-Cl-HCl.

Table 4
Peak assignments (cm⁻¹) and relative surface areas under each peak (%) observed during the adsorption of CO on the supported 0.6 wt%Pt–x wt%Rh and 0.3 wt%Rh/Al₂O₃ catalysts.

Catalyst	Linear on Rh ³⁺	Linear on Rh ²⁺	Gem sym on Rh ¹⁺	Linear on Pt ⁰	Pt–Rh alloy	Gem antisym on Rh ¹⁺
Rh/Al ₂ O ₃	2175 2.2%	2145 1.9%	2103 62.6%	–	–	2032 33.3%
Pt–0.30Rh/Al ₂ O ₃ -Cl	–	–	2103 4.3%	2082 44.2%	–	2032 51.5%
Pt–0.36Rh/Al ₂ O ₃ -RM	–	–	2103 0.2%	2076 34.9%	2061 29.2%	2032 35.7%
Pt–0.30Rh/Al ₂ O ₃ -Cl-HCl	–	2132 0.1%	2103 2.8%	2076 31.6%	2059 21.4%	2039 44.1%

sented, this system being used in the present work as reference since Ir-based catalysts are known to be the most active and selective for naphthenic ring opening (RO) [8].

First, Fig. 6a shows that the blank treatment of the Pt/Al₂O₃ catalyst involves a drastic decrease in the platinum activity for MCP conversion. Thus, at 400 °C, the parent catalyst presents a conversion value equal to 50%, against around 10% for the blank catalyst. This behaviour is related to the enlargement of the Pt particles during the blank treatment as described previously. Nevertheless, the blank treatment does not modify the quantities of C1–C5 products and consequently the RO selectivity (Fig. 6b). Compared to platinum, monometallic Rh and Ir systems are much more active for MCP hydrogenolysis, but, as expected, only the Ir-based catalyst presents very high RO selectivity even at high MCP conversion (less than 2% of C1–C5 products are produced up to 90% of conversion). In their paper, McVicker et al. [8] obtained 10.4% of MCP conversion with a RO selectivity of 97% with 0.3 wt%Pt/Al₂O₃ at 350 °C and 52% of MCP conversion with a RO selectivity of 99% with 0.9 wt%Ir/Al₂O₃ at 275 °C, in similar experimental conditions, except the H₂/MCP molar ratio, which was lower (5 instead of 7.5) and the WHSV, which was equal to 15 h⁻¹ for the platinum catalyst and 30 h⁻¹ for the iridium one, instead of 12 h⁻¹ in the present study. In order to compare these results with ours, the turnover

frequencies (TOF) were calculated considering that the dispersion of the catalysts studied in [8] was similar to those of the catalysts of the present study, i.e. 75% of dispersion for the platinum catalyst and 85% for the iridium one. The calculations give a TOF of roughly 1611 h⁻¹ for the 0.3 wt%Pt/Al₂O₃ of [8] and 1673 h⁻¹ for our 0.6 wt%Pt/Al₂O₃ at 375 °C, and 4661 h⁻¹ for the 0.9 wt%Ir/Al₂O₃ of [8] and 3958 h⁻¹ for our 0.6 wt%Ir/Al₂O₃ at 275 °C, which can be considered as similar performances taking into account the differences in the experimental conditions.

As already observed in our previous study [19], the addition of rhodium to platinum by surface redox reaction promotes the activity of the latter, leading to MCP conversions for the bimetallic Pt–Rh/Al₂O₃-RM catalysts intermediate between those of monometallic Pt and Rh systems (Fig. 6a). The activity increases with the Rh content to reach values very close to those of monometallic catalysts containing rhodium or iridium. Moreover, from the addition of the lowest Rh content to platinum (0.11 wt%), a decrease of the C1–C5 products formation is observed (Fig. 6b). This beneficial effect on the RO selectivity increases with the Rh loading, reaching a plateau from a content of 0.36 wt%Rh. Finally, the bimetallic Pt–Rh/Al₂O₃-RM catalysts with the highest Rh contents present RO selectivities comparable to those of monometallic Ir-based catalyst. The bimetallic Pt–Rh catalysts synthesized by RM method

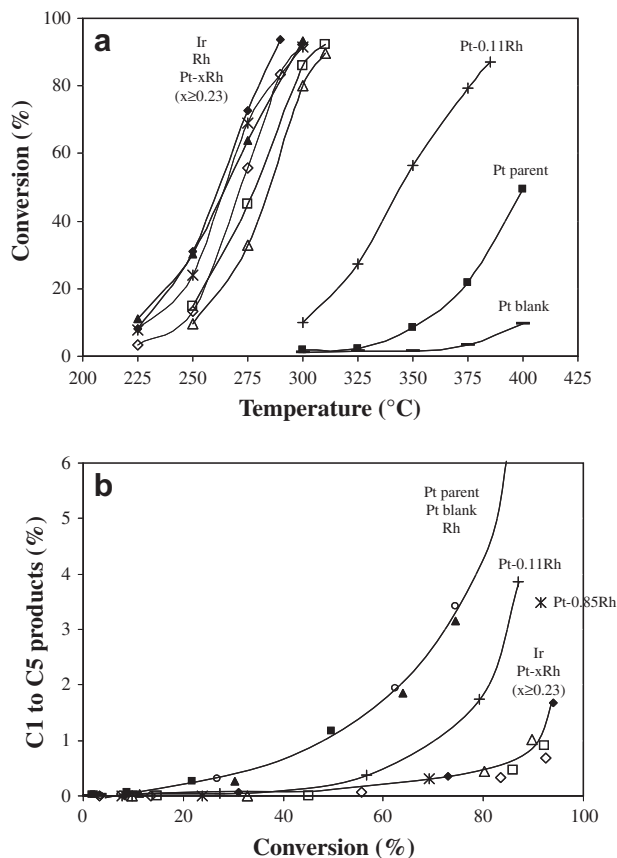


Fig. 6. (a) MCP conversion as function of temperature; (b) yield in C1–C5 products as function of the MCP conversion for the bimetallic Pt–Rh/Al₂O₃–RM series: (■) 0.6Pt/Al₂O₃–parent, (–) 0.6Pt/Al₂O₃–blank, (+) Pt–0.11Rh/Al₂O₃–RM, (Δ) Pt–0.23Rh/Al₂O₃–RM, (□) Pt–0.36Rh/Al₂O₃–RM, (◇) Pt–0.46Rh/Al₂O₃–RM, (∗) Pt–0.85Rh/Al₂O₃–RM. In addition: (▲) 0.6Rh/Al₂O₃, (◆) 0.6Ir/Al₂O₃, (○) experiment at WHSV = 6 h^{−1} performed with 0.6Pt/Al₂O₃–parent catalyst in order to complete the C1–C5 products curve shape of Pt-based systems.

are even more selective than the Pt–Rh systems prepared in our previous study by an alternative surface redox reaction [19], since the present RM method allows depositing higher Rh contents on Pt parent sample.

The RO product distribution and the molar ratio of *n*-hexane to 3-methylpentane (*n*-C6/3MP) and 2-methylpentane to 3-methylpentane (2MP/3MP) are gathered in Table 5 for the different catalysts, the values being given for MCP conversions as close as possible. However, previous results concerning platinum-based catalysts have demonstrated that for MCP conversions higher than 10%, the product distribution does not vary significantly as a function of the conversion [19]. Gault and et al. [40] showed that the ring opening product distribution results from three possible mechanisms: (i) a non-selective mechanism corresponding to an

equal probability of breaking cyclic bonds, and consequently to a statistical distribution with 2/5 of *n*-C6, 2/5 of 2MP and 1/5 of 3MP (i.e. *n*-C6/3MP and 2MP/3MP ratios both equal to 2); (ii) a completely selective mechanism producing only 2MP and 3MP, the breaking of substituted endocyclic C–C bonds being impossible (i.e. *n*-C6/3MP = 0 and 2MP/3MP = 2); (iii) a partly selective mechanism yielding to a product distribution intermediate between those obtained with the statistical mechanism and the selective one. According to the work of Weisang and Gault [41] and McVicker et al. [8], the MCP hydrogenolysis on the Ir/Al₂O₃ catalyst yields selectively to the formation of 2MP and 3MP (Table 5). On the Rh/Al₂O₃ catalyst, a selective mechanism is also observed with a very low percentage of *n*-hexane, in accordance with the results of Teschner et al. [42] and Coq et al. [43]. On the Pt/Al₂O₃ catalysts (parent and blank), the product distribution is close to 2/5 of *n*-C6, 2/5 of 2MP and 1/5 of 3MP. Consequently, in agreement with the results of McVicker et al. [8], the RO product distribution can be considered as resulting from a statistical mechanism, and no modification was induced by the blank treatment.

The addition of Rh loadings to platinum by RM method decreases the *n*-C6 formation, favouring the production of 2MP and 3MP. Consequently, for the bimetallic Pt–Rh/Al₂O₃–RM catalysts series, the *n*-C6/3MP ratios are close to 0 corresponding to a selective mechanism as for monometallic Ir- and Rh-based systems.

3.3.2. Comparison between the bimetallic Pt–Rh catalysts prepared by different methods

Thereafter, bimetallic Pt–0.30Rh/SiO₂–Cl, Pt–0.30Rh/Al₂O₃–Cl, Pt–0.30Rh/Al₂O₃–Cl–HCl and Pt–0.30Rh/Al₂O₃–Cl–T catalysts were tested in MCP ring opening in order to evaluate the influence of the preparation method, more exactly the influence of the bimetallic particles size on the RO performances. Compared to the Pt–Rh/Al₂O₃–RM sample with a similar Rh content (0.36 wt%), the Pt–0.30Rh/SiO₂–Cl catalyst presents the same activity curve for MCP conversion, whereas lower conversions were observed for the Pt–0.30Rh/Al₂O₃–Cl system (Fig. 7a). Nevertheless, the MCP conversions obtained on this last catalyst are still higher than those of the monometallic Pt/Al₂O₃ catalyst. The two treatments (HCl and T) performed on the Pt–0.30Rh/Al₂O₃–Cl sample lead to an increase of its activity, more particularly after the thermal treatment.

Concerning the RO selectivity, the Pt–0.30Rh/SiO₂–Cl catalyst presents a similar behaviour than that of the Pt–0.36Rh/Al₂O₃–RM system, with C1–C5 product percentages lower than 2% for more than 90% of conversion (Fig. 7b). On the other hand, the Pt–0.30Rh/Al₂O₃–Cl catalyst displays RO selectivities comparable or even lower than those of the monometallic Pt or Rh systems. The sintering of the metal particles of this bimetallic catalyst, induced by “HCl” or “T” treatment, allows improving the RO selectivity by decreasing significantly the formation of C1–C5 products at high MCP conversions.

Finally, all these observations highlight that the catalytic performances of the bimetallic Pt–Rh catalysts for MCP hydrogenolysis

Table 5

Yield in *n*-C6, 2MP, 3MP, *n*-C6/3MP and 2MP/3MP ratios on monometallic 0.6 wt%M/Al₂O₃ and supported bimetallic Pt–Rh catalysts prepared by refilling method (RM).

Catalyst	T (°C)	Conversion (%)	2MP (%)	3MP (%)	<i>n</i> -C6 (%)	<i>n</i> -C6/3MP	2MP/3MP
Ir/Al ₂ O ₃	275	73	68	29	3	0.1	2.4
Rh/Al ₂ O ₃	275	64	62	30	8	0.3	2.1
Pt/Al ₂ O ₃ –parent	400	50	45	23	32	1.4	1.9
Pt/Al ₂ O ₃ –blank	400	10	44	24	32	1.7	1.9
Pt–0.11Rh/Al ₂ O ₃ –RM	350	54	72	22	6	0.3	3.3
Pt–0.23Rh/Al ₂ O ₃ –RM	275	34	74	22	4	0.2	3.4
Pt–0.36Rh/Al ₂ O ₃ –RM	275	45	75	21	4	0.2	3.6
Pt–0.46Rh/Al ₂ O ₃ –RM	275	56	75	21	4	0.2	3.6
Pt–0.85Rh/Al ₂ O ₃ –RM	275	69	75	21	4	0.2	3.5

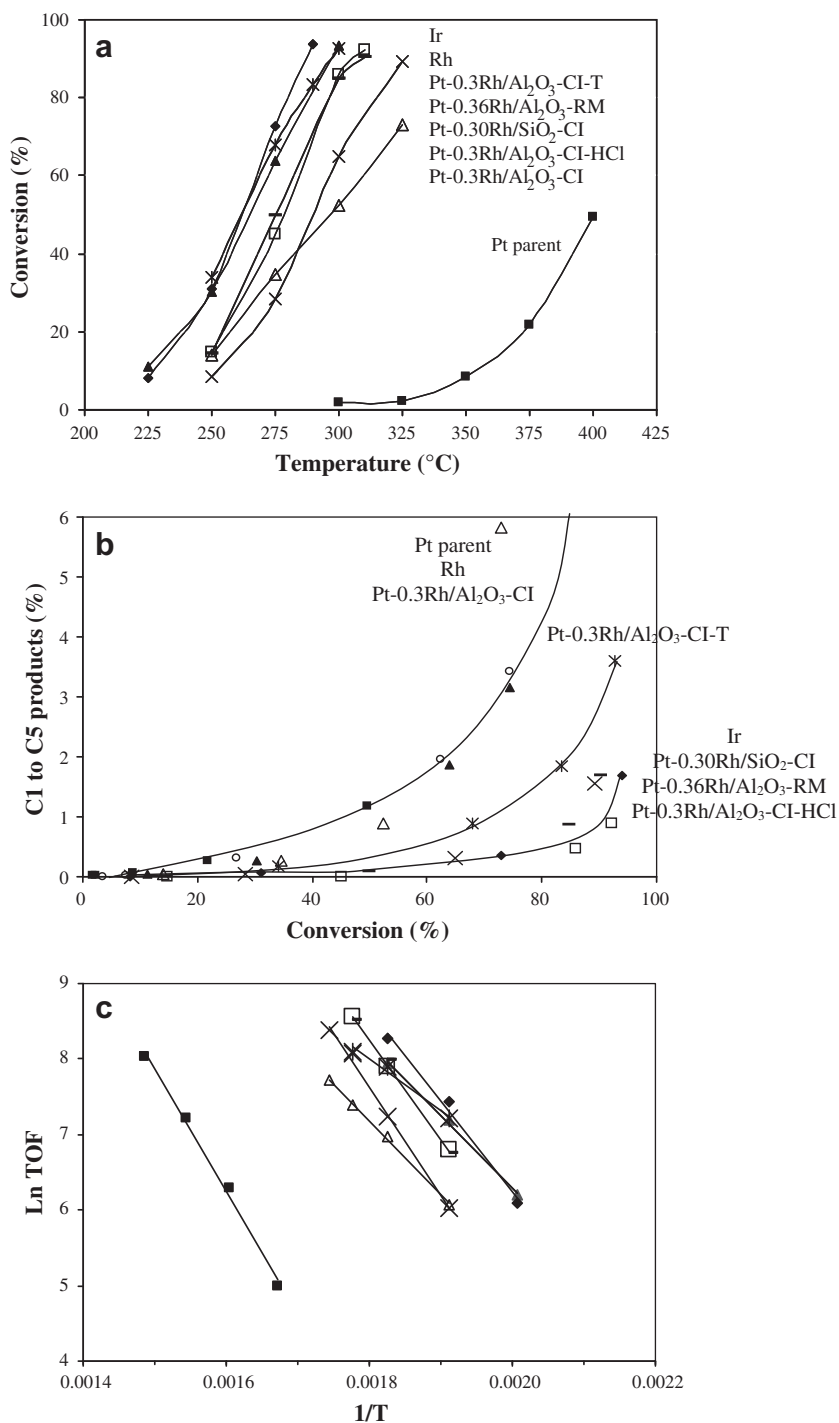


Fig. 7. (a) MCP conversion as function of temperature; (b) yield in C1–C5 products as function of the MCP conversion; (c) Arrhenius plot with TOF in h^{-1} and T in K for the supported bimetallic 0.6Pt–Rh catalysts prepared by various methods: (■) 0.6Pt/Al₂O₃-parent, (-) Pt-0.30Rh/SiO₂-CI, (△) Pt-0.30Rh/Al₂O₃-CI, (□) Pt-0.36Rh/Al₂O₃-RM, (*) Pt-0.30Rh/Al₂O₃-CI-T, (X) Pt-0.30Rh/Al₂O₃-CI-HCl. In addition: (▲) 0.6Rh/Al₂O₃, (◆) 0.6Ir/Al₂O₃, (○) 0.6Pt/Al₂O₃-parent at WHSV = 6 h^{-1} .

are closely linked to their preparation procedure that modulates deeply their average particles size and then the bimetallic particles structure. In Fig. 7b, the most selective bimetallic Pt–Rh catalysts for the MCP RO are the Pt-0.36Rh/Al₂O₃-RM, Pt-0.30Rh/SiO₂-CI and Pt-0.30Rh/Al₂O₃-CI-HCl catalysts, with RO selectivity comparable to that of Ir/Al₂O₃ sample. These three bimetallic catalysts present the largest particles size among all the prepared Pt–Rh systems (1.7–2.3 nm, Tables 1 and 2). Moreover, the previous characterizations have shown rather close behaviours for these three samples: (i) similar activities during cyclohexane dehydrogenation

(Fig. 2); (ii) similar H₂ consumption profiles during TPR experiments (Fig. 3B) and (iii) similar FTIR spectra of adsorbed CO (Figs. 4 and 5).

3.3.3. Study of the stability of the Pt–Rh catalysts prepared by refilling method

According to the previous results, the refilling method is a preparation procedure that directly allows synthesizing bimetallic Pt–Rh/Al₂O₃ catalysts as selective for the ring opening of methylcyclopentane as Ir-based catalysts for Rh content ≥ 0.23 wt%. Finally,

the stability of such bimetallic systems towards oxidation and under long operating conditions was evaluated and compared with that of a monometallic Ir catalyst.

First, in order to estimate the effect of an oxidation treatment onto the optimized bimetallic catalysts, the Pt–0.36Rh/Al₂O₃-RM and Pt–0.46Rh/Al₂O₃-RM catalysts were further submitted to calcination under air at 450 °C during 2 h followed by reduction at 500 °C under H₂ during 2 h. Fig. 8 gives the catalytic performances for MCP conversion obtained for the catalysts after such a treatment (notation: Pt–Rh/Al₂O₃-RM_{oxyd.}) compared with the fresh (not oxidized) ones and the monometallic Ir, Rh and Pt catalysts supported on alumina. Fig. 8a clearly shows that the oxidation treatment does not influence the activity of the Pt–Rh/Al₂O₃-RM catalysts for MCP conversion, since similar conversions are observed for fresh and oxidized catalysts. Moreover, the oxidation treatment does not modify the RO selectivity since the oxidized bimetallic catalysts lead to quantities of C1–C5 products still comparable with that of the monometallic Ir sample (Fig. 8b).

Secondly, the ring opening of MCP was performed on the Pt–0.36Rh/Al₂O₃-RM catalyst at 300 °C during 20 h of time-on-stream (TOS) in order to estimate its stability under long operating conditions. The results were compared with those obtained on the 0.6Ir/Al₂O₃ catalyst at 290 °C during the same period. Fig. 9 shows good stabilities as function of reaction time for both systems, i.e. no significant loss of MCP conversion and no significant evolution of the RO selectivity. Indeed, after 20 h of TOS, the bimetallic Pt–0.36Rh/Al₂O₃-RM catalyst always presents a conversion higher than 80% with less than 2% of C1–C5 products. Consequently, this bimetallic

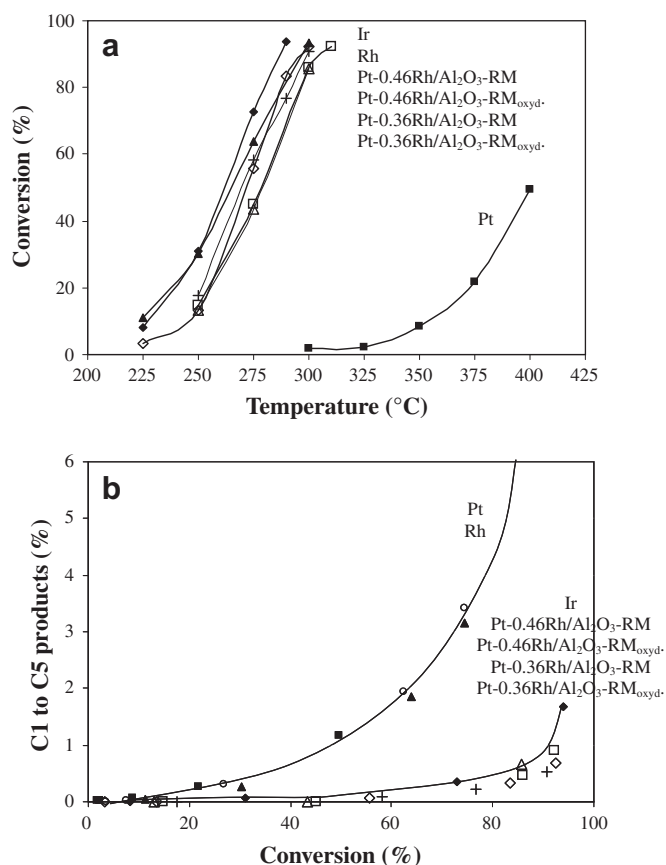


Fig. 8. (a) MCP conversion as function of temperature; (b) yield in C1–C5 products as function of the MCP conversion after oxidation treatment (specified by *oxyd.* index) of bimetallic Pt–Rh/Al₂O₃-RM catalysts: (△) Pt–0.36Rh/Al₂O₃-RM_{oxyd.}, (+) Pt–0.46Rh/Al₂O₃-RM_{oxyd.}, (□) Pt–0.36Rh/Al₂O₃-RM, (◇) Pt–0.46Rh/Al₂O₃-RM. In addition: (◆) 0.6Ir/Al₂O₃, (▲) 0.6Rh/Al₂O₃, (■) 0.6Pt/Al₂O₃.

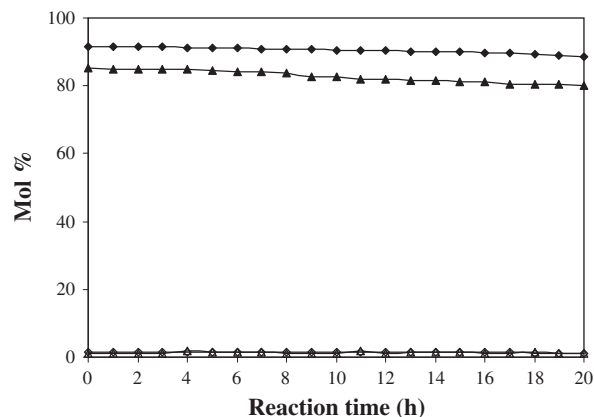


Fig. 9. Stability under long operating conditions of bimetallic Pt–0.36Rh/Al₂O₃-RM catalyst [mol% of (▲) converted MCP and (△) C1–C5 products] compared to 0.6Ir/Al₂O₃ catalyst [mol% of (◆) converted MCP and (◇) C1–C5 products].

system always presents high performances for selective ring opening of MCP even after long reaction time.

4. Conclusion

Our previous study [19] revealed that Pt–Rh/Al₂O₃ catalysts could be an interesting catalytic system for the ring opening of methylcyclopentane under pressure, since such samples prepared by a surface redox method showed RO selectivity higher than those of monometallic Pt/Al₂O₃ and Rh/Al₂O₃ systems, reaching the performances of an iridium-based sample tested in the same conditions. The present work was the continuation of this previous study, with the aim of characterizing supported bimetallic Pt–Rh samples prepared by various routes in order to understand the relationship between their structure properties and their catalytic performances for the MCP RO.

Two preparation methods were used to prepare Pt–Rh/Al₂O₃ and Pt–Rh/SiO₂ catalysts: (i) the refilling method RM (i.e. a surface redox reaction) performed in successive steps in order to obtain sufficient amounts of Rh deposited onto the monometallic Pt catalyst and (ii) the classical technique of coimpregnation CI. Varying the preparation procedure and the nature of the support leads to the formation of supported bimetallic Pt–Rh particles of different average size: >2.0 nm for all the catalysts except those synthesized on alumina support by CI method (1.2 nm). In order to obtain comparable sizes by the two preparation techniques, sintering treatments were performed on the latter inducing a slight enlargement of the particles.

The performances of the bimetallic Pt–Rh systems for RO of MCP were compared with those of monometallic catalysts containing iridium, rhodium and platinum in the same operating conditions under pressure. The bimetallic catalysts present an activity closed to that of Rh-based monometallic sample, whatever the preparation method (RM or CI), the support used (Al₂O₃ or SiO₂) and thus the average size of the metallic particles. The presence of a bimetallic Pt–Rh interaction was highlighted on all the prepared systems by various characterization techniques: by TEM coupled with EDX, by temperature-programmed reduction and by the probe reaction of cyclohexane dehydrogenation. However, the nature of the Pt–Rh phases differs according to the average particle sizes of the bimetallic sample. Indeed, cyclohexane dehydrogenation revealed the presence of a Pt surface enrichment on the largest bimetallic particles. It is known that under hydrogen atmosphere, the surface of bimetallic Pt–Rh particles is preferably enriched with platinum atoms, rhodium atoms being located in the

core, whereas the reverse is observed under oxidizing atmosphere [39,44–48]. But in the case of small particles (close to 1.0 nm), all the atoms are mainly located on the surface inhibiting this surface enrichment phenomenon. Moreover, FTIR of adsorbed CO showed that only the bimetallic particles of large enough size (>1.7 nm) present particular adsorption sites associated in the literature to the presence of a Pt–Rh alloy. During the MCP ring opening reaction, only these particles lead to RO selectivities comparable with that of iridium. Consequently, synthesizing Pt–Rh catalysts with bimetallic interactions does not lead systematically to catalytic systems as selective as Ir-based catalysts for MCP RO. The particle size seems to be a determining parameter that induces a different surface composition of the bimetallic particles. Finally, the presence of bimetallic particles of small sizes (≈ 1.0 nm) is not required, largest particles being more selective for MCP RO, leading to performances similar to those of iridium-based reference catalysts. In this context, the refilling method allows obtaining Pt–Rh/Al₂O₃ catalysts with the required structural properties, and moreover, these systems show a good stability towards oxidation and under long operating conditions, as well on the level of the MCP conversion as of the RO selectivity.

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