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# Aromatic Reduction Over Supported Modified Platinum Catalysts

## Influence of a Second Metal on the Sulfur Resistance of Platinum

E. Guillon<sup>1</sup>, B. Didillon<sup>2</sup> and D. Uzio<sup>1\*</sup>

<sup>1</sup> IFP -Lyon, BP 3, 69390 Vernaison - France

<sup>2</sup> Rhodia, PPD, PO Box 9837 Oldbury, West Midlands, B69 4WD - United Kingdom

e-mail: denis.uzio@ifp.fr – emmanuelle.guillon@ifp.fr

\* Corresponding author

**Résumé — Réduction des aromatiques sur catalyseurs à base de platine : influence d'un second métal sur la résistance au soufre** — Des catalyseurs bimétalliques de type  $Pt/M Al_2O_3$  avec  $M = Ge, Au$  ou  $Pd$  ont été préparés et caractérisés par titrage volumétrique  $H_2/O_2$  et spectroscopie IR(CO). Les effets d'un second métal sur la résistance au soufre du platine ont été suivis en hydrogénation de l'orthoxyène. Comparés au catalyseur platine monométallique de référence, les catalyseurs bimétalliques se classent en terme d'activité hydrogénante selon :  $PtPd > PtAu \geq Pt \gg PtGe$ . Le rapprochement entre ces résultats catalytiques et les propriétés électroniques obtenues à partir de l'IR(CO) ou de l'hydrogénation de l'orthoxyène sans soufre, montre que la résistance au soufre du platine ne peut pas être exclusivement reliée à un effet électronique et à une nature électrodéficiente des atomes de platine de surface. Le processus d'empoisonnement par le soufre sur ces systèmes est discuté.

**Abstract — Aromatic Reduction Over Supported Modified Platinum Catalysts: Influence of a Second Metal on the Sulfur Resistance of Platinum** —  $Pt-M/Al_2O_3$  bimetallic catalysts with  $M = Ge, Au$  or  $Pd$  were prepared and characterised by  $H_2-O_2$  volumetric titration and IR(CO) spectroscopy. The effects of the second metal on the sulfur resistance of platinum were investigated by the hydrogenation of orthoxyene. Compared to platinum monometallic reference catalyst, the bimetallic catalysts ranking in terms of hydrogenation activity was  $PtPd > PtAu \geq Pt \gg PtGe$ . Correlation between these catalysis results and electronic properties extracted from IR(CO), or orthoxyene hydrogenation without sulfur, shows that sulfur resistance of platinum can not be exclusively related to an electronic effect and an electrodeficient character of Pt surface atoms. The mechanism of sulfur poisoning is discussed.

## INTRODUCTION

High polyaromatics (anthracenes, naphthalenes, tetralins) content in diesel fuels has been recognised both to lower the fuel quality and to significantly contribute to the formation of particles and undesired emissions in exhaust gases. Due to health hazards associated with these emissions, environmental regulations governing the composition of diesel fuels are being tightened leading to limitations on aromatics. As a consequence, processes for aromatic reduction in such petroleum product by metal sulphide and noble metal catalysts have received considerable attention in recent years.

Supported platinum catalysts have demonstrated their capacity to exhibit high aromatic hydrogenation activity but they suffer from a great sensitivity to sulfur present in the feedstocks [1, 2]. Therefore, extensive research has been undertaken to develop sulfur resistant platinum catalysts.

Origins of the sulfur resistance of supported metal catalysts are often ascribed in the literature to the electron deficient nature of surface metal atoms which leads to a decrease of the sulfur-metal bond strength [3-8].

The electron deficient character of the metal can be obtained through two main ways:

- by playing with the nature of the support; sulfur resistance of metals supported on acidic supports, such as zeolite or modified alumina has been widely reported in the literature [9-13];
- by adding a specific modifier such as a second metal which confer to the platinum specific characteristics. Addition of a second metal (*Ge* [14], *Ir*, *Re*, *Pd* is one of the most studied [15-17]) or combination of both approaches [18] can markedly improve the catalytic performance of alumina supported platinum catalysts for the reduction of aromatics in diesel fuels, in presence of sulfur compounds.

At present, due to the catalysts preparation methods, the different metallic structures obtained (alloys, solid solution, segregation, divided metal particles, etc.), the different ways to consider the sulfur resistance (quantity of adsorbed sulfur, toxicity, residual activity, slope of deactivation, etc.), the various operating conditions lead to have an unclear description of the phenomenon and contradictions still remain in the literature on this topic [19-22].

The objective of this study is to add to the understanding, for different platinum based bimetallic catalysts, of the relationship between electronic properties of platinum and the sulfur resistance of catalysts. To achieve this goal, we chose three bimetallic systems where the second metal may induce opposite electronic effects to platinum, at least regarding their Pauling electronegativity (*Table 1*).

Bimetallic catalysts *Pt-Ge*, *Pt-Au* and *Pt-Pd* [11, 12, 24-26] supported on alumina have been already studied in literature for various refining and petrochemical applications.

These systems are likely to present some thioresistance properties (case of *Pt-Pd*) or electrodeficiency of platinum (case of *Pt-Ge* [27]), supporting their selection for our study.

TABLE 1  
Pauling Electronegativity [23]

Element	Electronegativity
<i>Pt</i>	2.28 eV
<i>Pd</i>	2.20 eV
<i>Ge</i>	2.01 eV
<i>Au</i>	2.54 eV

For catalysts preparation, organometallic precursors have been used in order to control interaction between metals as described for others systems [28]. The key point is to prepare catalysts that are homogeneous in terms of particle size and bimetallicity at the particle scale.

The catalysts have been first characterised in terms of dispersion using probe molecule adsorption ( $H_2$ ,  $O_2$ ). Studies have been focused on catalysts having particle size in the same range in order to separate particle size and modifier effects.

Electronic modifications of platinum have been checked using methods described in literature: infrared spectroscopy of adsorbed carbon monoxide [29] and selectivity in the trans-dimethylcyclohexane of orthoxylene hydrogenation reaction [30, 31].

The sulfur resistance of the catalysts characterised as described above has been determined under representative conditions using orthoxylene as the aromatic molecule in presence of sulfur. On the basis of these results, the impact of electronic modification of platinum on the sulfur resistance of catalysts is discussed.

## 1 EXPERIMENTAL

### 1.1 Preparation of Catalysts

The support used was a  $\gamma$  alumina with a specific surface area of 200  $m^2/g$  and a pore volume of 0,6  $g/cm^3$ . The support is in the form of beads of 2 mm average diameter. The support activation is performed under air flow during 2 h at 350°C, in order to confer the appropriate alumina surface properties.

The monometallic catalysts, *Pt1* and *Pt2*, called “parent catalysts” are obtained by an excess impregnation of alumina using platinum bis-acetylacetonate in toluene according to the procedure described in ref. [28]. The impregnation was carried out at room temperature under steady-state conditions for 72 h. After filtration, the catalyst was dried for 12 h at 120°C, calcined for 2 h at 350°C and then reduced under hydrogen at 450°C. The catalyst *Pt1* contains 1 wt% of *Pt*; *Pt2* contains 1,3 wt% of *Pt*.

Modified platinum catalysts  $Pt\text{-}M/\text{Al}_2\text{O}_3$  were prepared with a molar ratio  $M/\text{Pt} = 1$ , starting from the monometallic parent catalysts  $Pt1$  and  $Pt2$ , according to the following procedures:

$PtGe$  catalyst was prepared by the method of incipient wetness impregnation. The parent monometallic catalyst was impregnated with appropriate amount of tetra-*n*-butyl germane  $Ge(\text{C}_4\text{H}_9)_4$  dissolved in *n*-heptane. After drying 12 h at 120°C, the catalyst is reduced 2 h at 450°C under hydrogen flow. Direct reduction avoids loss of volatile  $GeO$  during the calcination and enables a good interaction between platinum and germanium [32].

A germanium monometallic catalyst was prepared by incipient wetness. The catalyst containing 0,3 wt% germanium is referred to as  $Ge$ .

$PtAu$  catalyst was prepared from a solution of chloroauric acid  $\text{HAuCl}_4$  according to the method described by Barbier [33]. After the reduction of the parent monometallic  $Pt$  catalyst, the sample is transferred under nitrogen flow in a reactor filled with aqueous gold chloroaurate solution. This solution is first purged in argon for 30 min before transfer of the catalyst.  $\text{AuCl}_4^-$  ions on the monometallic catalyst use hydrogen adsorbed on the platinum particles as reducer. After 30 min under inert atmosphere,  $\text{H}_2$  flow is established during 30 min. Finally, the catalyst is washed with water in order to remove unreacted gold anions, dried 12 h at 120°C, calcined 2 h at 350°C under air and reduced 2 h at 450°C under hydrogen flow. This catalyst, referred to as  $PtAuCl$ , contains a small amount of chlorine which may affect sulfur resistance [11]. Dechlorination is performed by washing the catalyst with  $\text{NH}_3$  (0,01 N) in order to keep a Cl loading lower than 100 ppm. The catalyst is called  $PtAu$ .

$PtPd$  catalyst is prepared by decomposition of an organometallic precursor on a monometallic parent catalyst according to the following procedure: the catalyst parent  $Pt2$  is reduced under hydrogen flow at 350°C. The catalyst is then transferred into toluene containing palladium acetylacetonate under nitrogen. After 2 h, the catalyst is washed, dried 12 h at 120°C, calcined 2 h at 350°C under air flow and reduced 2 h at 450°C under hydrogen.

Finally, a monometallic catalyst  $Pd/\text{Al}_2\text{O}_3$ , referred to as  $Pd$ , containing 0,8 wt%  $Pd$  has also been prepared by excess impregnation from palladium acetylacetonate.

The main characteristics of all the catalysts are given in Table 1.

## 1.2 Characterization

### 1.2.1 $\text{H}_2\text{-O}_2$ Volumetric Titration

Experiments were performed using a  $\chi$ -sorb apparatus. After reduction of catalysts at 450°C, the chemisorbed hydrogen was titrated by oxygen pulses at 30°C. A second titration was done after a 30 min reduction under hydrogen at 30°C. A

stoichiometry of one atom of hydrogen per atom of  $Pt$  and  $Pd$  was used to determine the percentage of accessible metal.

### 1.2.2 Infrared Spectroscopy Coupled with CO Chemisorption (IR(CO))

IR(CO) was carried out by a DIGILAB FTS80 interferometer. The sample (20 mg) was pressed as a disk under 200 kg/m<sup>2</sup> and placed in an *in situ* cell. The disk diameter was 16 mm. A thermal treatment was applied in the following conditions: reduction under hydrogen at 450°C (2h), cooling to 30°C under secondary vacuum ( $4.10^{-6}$  Torr), then at 30°C, introduction of 30 mbar of CO. A dispersion of CO molecules was obtained by heating the sample to 100°C during 15 min under CO pressure. The sample was then heated by steps under secondary vacuum at 30°C for 1 h and at 100°C, 240°C, 340°C, 380°C during 30 min until total CO desorption was obtained. After each step, spectra were obtained at room temperature in transmission mode with an accumulation time of 100 s and a resolution of 4 cm<sup>-1</sup>.

## 1.3 Catalytic Tests

Orthoxylene hydrogenation reaction was chosen as a test reaction and performed with and without addition of a sulfur compound in the feed.

### 1.3.1 Without Sulfur Addition

The test was performed in a continuous fixed-bed reactor under atmospheric pressure. A quartz reactor with a volume of 80 cm<sup>3</sup> and a diameter of 2.5 cm was used. Samples dispersed in SiC were reduced at 450°C under hydrogen before catalytic tests. The feed is composed by 10% volume of orthoxylene in *n*-heptane. The operating conditions were as follows: 2 g of catalyst, 100°C, 120 ml/h of feed and 6 l  $\text{H}_2$ /h. They were adjusted to maintain less than 10% of orthoxylene conversion, to avoid any isomerization of the products.

### 1.3.2 With Addition of Sulfur Compounds

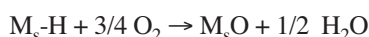
The test was performed in a continuous fixed-bed reactor under a total pressure of 40 b. The volume of catalyst was 20 cm<sup>3</sup> without SiC. Feed was composed of 10%wt of orthoxylene in *n*-heptane as solvent. 100 ppm of sulfur was added as Dimethyl Disulphide (DMDS). The operating conditions are as follows: 10 h at  $T = 100^\circ\text{C}$ , 20 l  $\text{H}_2$ /h, LHSV = 7 h<sup>-1</sup> then 20 h at 20 l  $\text{H}_2$ /h at  $T = 100^\circ\text{C}$  and LHSV = 1 h<sup>-1</sup>. In these conditions, DMDS is completely decomposed to  $\text{H}_2\text{S}$ . The aim of the first ten hours is to quickly stabilize the catalyst in order to study, in a second step, the residual activity of the catalyst in presence of the same amount of sulfur.

The products were analysed by a Hewlett Packard gas chromatograph with PONA column (temperature program: 90°C to 130°C, heating rate 2°C/min).

## 2 RESULTS

### 2.1 Platinum Accessibility

After a 450°C reduction under hydrogen of the catalyst, the first titration gives the oxygen volume needed to react with chemisorbed hydrogen atoms on the reduced metal atoms (*Pt* or second metal) according the following equation:



Gold and germanium do not adsorb oxygen and hydrogen at room temperature. So, after the 30°C reduction, except for the *PtPd* catalyst, only reduced surface platinum  $Pt_s$  is available for titration. A stoichiometry of one atom of hydrogen per atom of platinum is used to determine the accessibility of platinum.

In Table 3 are reported the measured oxygen volume for the two titrations and the metal accessibility (% relative error = 5%).

In the case of the highly dispersed monometallic platinum catalyst, the adsorbed oxygen volume is the same for the two temperatures. This is observed in particular for the parent catalyst *Pt1* and *Pt2* (78-79% platinum accessibility for the two titrations). This dispersion corresponds to an average platinum particle size of 10 Å. This value was confirmed by transmission electronic microscopy.

For *PtGe* catalyst, the oxygen volume obtained for the two titrations is different. The first titration volume is higher and the difference with the second titration can be ascribed to the participation of a fraction of reduced germanium at 450°C, as suggested by Garetto and Borgna [20]. As germanium does

not adsorb hydrogen at room temperature [24], for *PtGe* catalyst, the second titration gives the sole platinum accessibility. As we can see, addition of germanium does not change significantly the platinum accessibility, respectively 74% and 78% for *Pt1*. This result is in agreement with the studies by Goldwasser [34]. We can conclude that as far as the titration technique is considered, the particle size did not change by germanium addition. This result was confirmed by transmission electron microscopy.

Concerning the *PtAu* system, the first and second titration values lead to the same oxygen volume. As gold keeps its metallic form (oxidation degree = 0) for the two temperatures, the two titration volumes are characteristic of total metallic accessibility including platinum and gold surface atoms. The amount of chemisorbed oxygen is smaller than that obtained for the parent catalyst *Pt1*, which shows a decrease of platinum accessibility in presence of gold. This result is consistent with the preparation method where gold is deposited onto reduced platinum. This agrees with literature data where gold is supposed to have a geometrical effect on platinum [35].

In the case of *PtPd* catalyst, the oxygen volumes are similar for the two measurements. As the probe molecules (oxygen and hydrogen) can be chemisorbed on the two metals (platinum and palladium), we determine by this method the overall accessibility of metal atoms. The accessibility is the same in the first and second titration. The metal accessibility of *PtPd* decreases compared to monometallic *Pt2* and *Pd* (45% for 79%), showing that the palladium is not deposited on the support. In the opposite case, the accessibility would have been unchanged (80%). The estimated particle size is 15-20 Å, with good agreement with transmission electron microscopy.

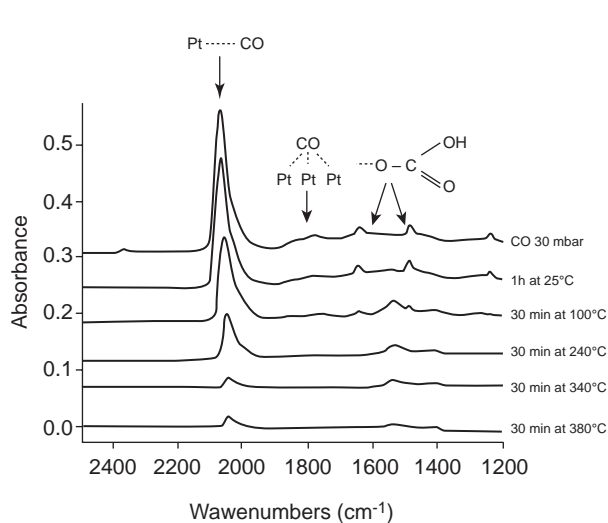


Figure 1  
IR(CO) spectra for the *Pt* catalyst.

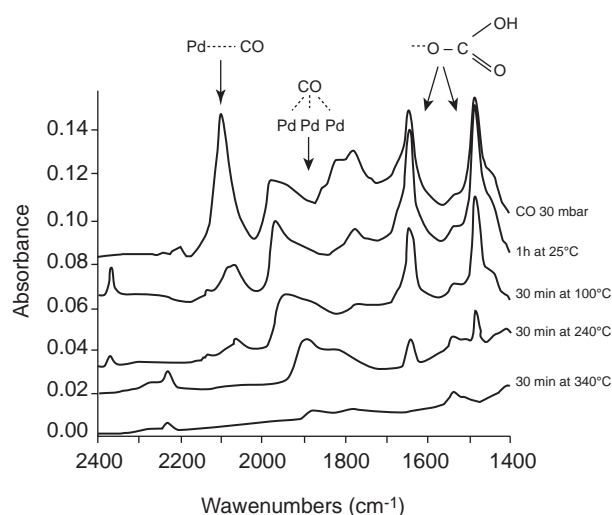


Figure 2  
IR(CO) spectra for the *Pd* catalyst.

TABLE 2  
Volumetric H<sub>2</sub>-O<sub>2</sub> titration results

Catalysts	Volume of oxygen adsorbed (ml/g) V <sub>1</sub> /V <sub>2</sub>	Accessibility (%) 450°C/30°C
<i>Pt1</i>	0.8/0.8	78/78
<i>Pt2</i>	1.0/1.0	78/79
<i>Ge</i>		
<i>PtGe</i>	0.8/0.7	86/74
<i>PtAuCl</i>	0.6/0.7	60/63
<i>PtAu</i>	0.5/0.6	62/66
<i>PtPd</i>	0.9/0.9	45/45
<i>Pd</i>		80*

\* CO chemisorption.

TABLE 3  
IR(CO) results

Catalyst	n(CO) at lowest CO coverage (cm <sup>-1</sup> )
<i>Pt1</i>	2039
<i>PtGe</i>	2051
<i>PtAuCl</i>	2043
<i>PtAu</i>	2039
<i>PtPd</i>	2032
<i>Pd</i>	2063

## 2.2 Electronic Effects

Infrared spectroscopy coupled with CO chemisorption allows the study of electronic modification induced by the second

metal on the surface platinum atoms through the frequency shift of the stretching vibration of linearly adsorbed CO. To avoid dipole-dipole interactions,  $\nu(\text{CO})$  frequencies were measured at lowest CO coverage, close to zero. This was obtained by thermodesorption of an excess of initially adsorbed CO. The results will be discussed in terms of wavenumbers  $\bar{\nu}\text{CO}$ . The wavenumbers of CO adsorbed linearly on platinum at lowest CO coverage  $\bar{\nu}\text{CO}$  are given in Table 3 for all the catalysts (accuracy of measurement =  $\pm 2\text{ cm}^{-1}$ ).

Figure 2 shows an example of thermodesorption profile (case of *Pt1*) where the adsorbed CO species are described (linear and bridged CO adsorbed). It shows the decrease of  $\bar{\nu}\text{CO}$  of linear CO adsorbed on platinum versus the CO coverage.

For the monometallic Pt catalyst,  $\bar{\nu}\text{CO}$  is 2039 cm<sup>-1</sup> at lowest CO coverage (Table 3). Germanium and gold do not adsorb CO at ambient temperature.

Addition of Ge (*PtGe*) leads to a band wavenumber shift of + 12 cm<sup>-1</sup> (from 2039 for *Pt* to 2051 cm<sup>-1</sup> for *PtGe*) at lowest and highest CO coverage (Figure 3a shows for *PtGe* catalyst the evolution of CO versus CO coverage). This shows that germanium does not have a geometric effect on platinum, in agreement with the absence of modification of platinum accessibility by adding germanium (titration results).

According to the Blyholder model, the electronic interpretation of the shift is a decrease in the electronic density of platinum lowering the retrodonation [36], leading to a strengthened CO bond and a higher CO adsorbed wavenumber. Bowman and Biloen [27] have already shown this tendency towards electrodeficient platinum atoms when alloyed with germanium by an XPS study.

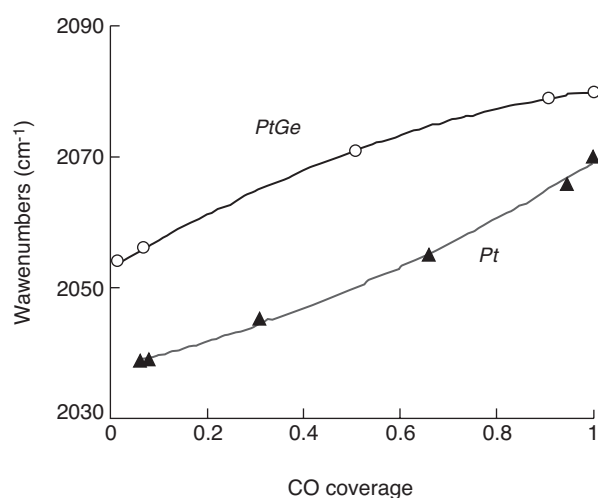


Figure 3a  
Evolution of CO for *PtGe* and *Pt* as a function of CO coverage

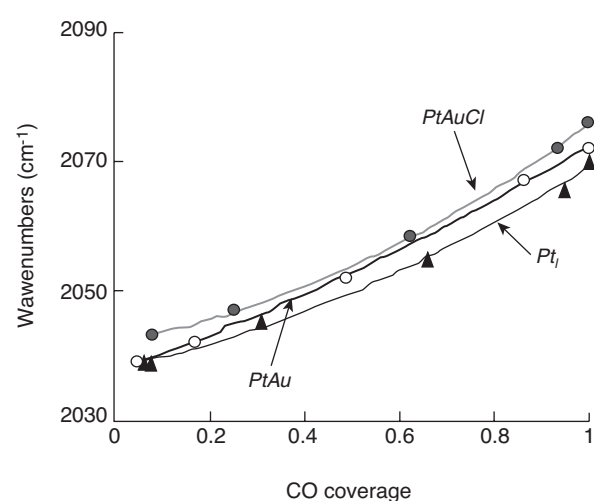


Figure 3.b  
Evolution of CO for *PtAu*, *PtAuCl* and *Pt* as a function of CO coverage.

No wavenumber shift was measured at lowest CO coverage for *PtAu* (Fig. 3b, Table 3). Gold has consequently no electronic effect on platinum. This is consistent with the geometrical effect proposed on the basis of volumetric titration results. A shift of + 4 cm<sup>-1</sup> was detected for *PtAuCl* (2043 cm<sup>-1</sup>) compared to *Pt* (2039 cm<sup>-1</sup>). It is likely to come from the presence of chlorine, which is well known to modify the electronic properties of platinum atoms [37].

For the study of *PtPd* catalysts, the interpretation of the results is more difficult because we must consider that *Pd* adsorbs linear and bridged CO (Fig. 4). The intensity of bridged *Pd*-CO bands is decreased for *PtPd* compared to *Pd* catalyst. The diluting of the number of adsorption sites, which contains adjacent Pd atoms, is probably the main reason of this observation. Nevertheless, the existence of bridged *Pd*-CO involves the presence of adjacent palladium atoms on the metallic surface. This is likely due to the preparation method, by deposition of palladium on platinum.

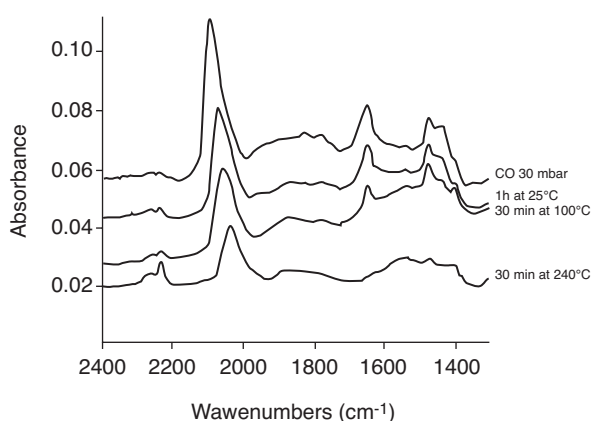


Figure 4  
IR(CO) for the *PtPd* catalyst.

CO linearly adsorbed on platinum is much more strongly held than CO linearly adsorbed on palladium: the lowest CO coverage is obtained for lower desorption temperature on palladium (see Fig. 1 and 2). The vibration frequencies of these two species are very close and difficult to separate for *PtPd* systems. For *PtPd*, the measured frequency decreases with CO coverage and is lower than that measured for the monometallic platinum catalyst at lowest coverage (2039 cm<sup>-1</sup> for *Pt* and 2032 cm<sup>-1</sup> for *PtPd*, Table 3). According to Grill [38] the absorbance of CO linearly adsorbed on platinum is measured at lowest coverage and the absorbance of CO linearly adsorbed on palladium at higher coverage. Nevertheless, this hypothesis does not take into

account the CO-CO interactions at high coverage and the possible modification of CO adsorption on palladium in the bimetallic *PtPd* phase. Indeed, these factors might strongly influence  $\nu(\text{CO})$ . Furthermore, the preferential adsorption of CO on platinum compared to palladium, studied and observed by Radosavkic [39], and the possible surface segregation of the palladium makes interpretation of the IR(CO) results difficult. This phenomenon may explain the contradictions observed in the literature concerning the characterisation of *PtPd* catalysts by IR (CO) [46, 40, 41].

Orthoxylene hydrogenation has been described as a reaction allowing electronic interactions in bimetallic catalysts to be followed [28, 42, 51]. As shown in several studies, the selectivity towards trans-DMCH is linked to the electron density of the metal. Indeed, the trans-selectivity is used as a probe of electronic properties of *Pt* atoms: if the trans-selectivity increases, metal atoms have an electro-deficient character.

It was checked that the reaction was not diffusion limited by determining the apparent activation energy of 9 kcal/mol, which is in agreement with precedent studies [43].

Results are expressed by rate constant ( $gPr^{-1} h^{-1}$ ) assuming a pseudo 1<sup>st</sup> order with respect to the aromatic. Rate constant and selectivities toward trans-dimethylcyclohexane (trans-DMCH) are presented in Table 4.

Ge and Au monometallic catalysts are not active for aromatic hydrogenation. *Pd* monometallic activity is very low compared to *Pt* (hydrogenation rate constant is  $4.10^{-3} h^{-1}.g^{-1}$  for *Pd* and  $230.10^{-3} h^{-1}.g^{-1}$  for *Pt2*) and selectivity is very high compared to *Pt* (70% for 31%).

For *PtGe*, the activity of the catalyst decreases with addition of germanium and the trans-DMCH selectivity increases from 31% for *Pt* to 50% for *PtGe*. This result suggests an electro-acceptor effect of germanium towards platinum.

In presence of gold, the platinum activity decreases whereas the selectivity remains the same (30% for *PtAu* and 31% for *Pt*). This is in agreement with a geometrical effect of gold on platinum, which decreases the platinum accessibility and does not modify the electronic properties of platinum. In presence of chlorine, the activity is better compared to *PtAu*, the same compared to *Pt* and the selectivity is almost the same.

For the *PtPd* catalyst tested for orthoxylene hydrogenation, the resultant activity is lower than the sum of *Pt* and *Pd* individual activities. Moreover, the selectivity towards the trans isomer is always higher when compared with *Pt*. This increase of selectivity suggests an electrodeficient character of platinum in presence of palladium. As the selectivity of monometallic *Pd* is high, it could be also responsible of the selectivity value; nevertheless an additive effect is not possible because the platinum activity is not conserved.

The interpretations of the IR(CO) and TDMCH selectivity results, used to study electronic properties, are in agreement

concerning the *PtGe* particles, leading to electron deficient platinum atoms.

The understanding of *PtPd* system is more delicate, probably because of an additional phenomenon: surface segregation of palladium atoms. Indeed, results must be related to the true surface composition in terms of *Pt* and *Pd* atoms. Regarding the selectivity during orthoxylene hydrogenation, platinum is electrodefficient in presence of palladium.

TABLE 4

Catalytic results for hydrogenation of orthoxylene without sulfur on Pt-M supported catalysts.

Catalyst	Conversion 5%°	constant rate (h <sup>-1</sup> . g <sup>-1</sup> Pt × 10 <sup>3</sup> )	trans-DMC6 Selectivity (%)
<i>Pt2</i>	6.0	230	31
<i>Pd</i>	0.1	4	69
<i>PtGe</i>	0.1	10	48
<i>PtAuCl</i>	4.3	190	31
<i>PtAu</i>	3.0	160	30
<i>PtPd</i>	0.8	30	43

TABLE 5

Sulfur resistance results- 100 ppm of S- Operating conditions: VVH = 1; T = 200°C

Catalysts	Conversion (%)	Rate constant (h <sup>-1</sup> . g <sup>-1</sup> Pt × 10 <sup>3</sup> )
<i>Pt2</i>	3.5	3.0
<i>PtGe</i>	0	0
<i>PtAu</i>	4.0	4.4
<i>PtAuCl</i>	10.9	9.6
<i>PtPd</i>	7.5	6.7
<i>Pd</i>	0.4	0.6

### 2.3 Catalytic Results in Presence of Sulfur

The sulfur resistance of the different catalysts is studied by comparison of the hydrogenation rate to that of the monometallic platinum catalyst. The results are presented Table 5.

Without sulfur, the monometallic palladium catalyst displays a lower hydrogenation activity than platinum (activity ratio *Pt/Pd* = 50). In presence of sulfur, *Pd* activity remains very low, lower than *Pt* monometallic catalyst (activity ratio *Pt/Pd* = 5). So, the sulfur sensitivity of aromatic hydrogenation on palladium is lower than for platinum if we compare the activity with and without sulfur.

Germanium increases platinum sulfur sensitivity and the catalyst is fully deactivated during the second step (see Table 5). The platinum activity could not be retained in presence of germanium.

*PtAu* slightly improves the sulfur resistance of platinum ( $4.4 \times 10^{-3}$  compared to  $3 \times 10^{-3}$  mol/h.g *Pt*). For *PtAuCl*, the platinum activity is still further improved ( $9.6 \times 10^{-3}$  mol/h.g *Pt*): the presence of chlorine improves the thioresistance, as already shown [11].

Palladium improves platinum sulfur resistance. Indeed, the hydrogenation rate is doubled for *PtPd* and reaches  $6.7 \times 10^{-3}$  mol/h.g *Pt* compared to  $3 \times 10^{-3}$  mol/h.g *Pt* for *Pt*.

## DISCUSSION

The objective of this study is to bring new insights on the relationship between electronic properties of platinum and sulfur resistance of catalysts. To achieve this goal, we chose three bimetallic systems where the second metal may induce opposite electronic effects on platinum, at least regarding their Pauling electronegativity.

The three bimetallic catalytic systems present different physical and catalytic properties. As shown by CO chemisorption coupled with IR and orthoxylene hydrogenation, germanium acts as an electro-acceptor toward platinum. Nevertheless, contrary to what would be expected considering the literature [14-20] germanium does not improve the sulfur resistance of platinum and furthermore platinum does not keep its own activity in presence of germanium.

Gold, which has mainly a geometrical effect on platinum, does not play a significant role on platinum thioresistance. The geometric effect on platinum is not a key parameter for platinum thioresistance improvement.

The *PtPd* system gives the best hydrogenation activity in presence of S; the palladium has a positive effect on platinum sulfur resistance, although Pd monometallic catalyst is not a good hydrogenation catalyst.

To explain the poor sulfur resistance of *PtGe*, we can take into account that aromatic hydrogenation is also linked with the nature of electronic density of platinum. It is well known that adsorption strength of hydrocarbons are modified by electronic modification of the metal [44, 45]. The metal's electronic properties change the adsorption strength between the aromatic compound and the metallic site and consequently the hydrogenation activity following the Sabatier principle. This point has to be considered here to explain the sulfur resistance for aromatic hydrogenation.

In the case of the *PtGe* catalyst, aromatic cycles are more strongly adsorbed on electrodefficient platinum and the aromatic molecule poisons the metallic surface sites, blocking the reaction: the o-xylene hydrogenation activity decreases in presence of germanium. In presence of sulfur which has an electroacceptor character [3], platinum is all the more electrodefficient and this kills the residual hydrogenation activity. In this qualitative approach, which takes into account the effect of adsorbed sulphur and aromatic adsorption strength, considering only the electrodefficiency of platinum is not enough to explain sulfur resistance.



Concerning PtPd systems, sulfur resistance may come from a specific structure of PtPd alloy (core-shell like structure). In fact, it has been shown that, in bimetallic alloyed PtPd particles, Pd segregates from the bulk to the surface of aggregates [46-51] especially on low coordination (for the most part edge and corner) sites [46]. Indeed, it has been demonstrated on platinum monocrystals that sulfur adsorbs preferentially on these types of sites [3], which are known to be more electro-enriched. Preferential adsorption of sulfur on palladium segregated at the surface might explain the sulfur resistance of PtPd. Moreover, electronic modifications of Pd surface atoms by the subsurface Pt lead to the optimal adsorption strength of the reactants in presence of sulfur.

## CONCLUSION

The correlation between platinum electronic properties and catalytic data allows us to state that the electrode deficient character of platinum is not only the parameter needed to explain the sulfur resistance properties. Parameters such as chemical bonding strength of S and aromatic on the metallic site and characteristics of bimetallic aggregates (structure and surface composition) have to be considered.

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