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ON THE SPECIFIC REACTIVITY OF PLATINUM SEGREGATED LAYERS ON $Pt_{80}X_{20}$ (111) (X = Ni, Co, Fe) ALLOYS

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The influence of alloying of Pt with 20 at.% of Ni, Co and Fe has been studied in the hydrogenation of 1,3 butadiene. Iron induces the more important modifications, with both higher activity and selectivity. The results are discussed in terms of the surface segregation, the local order in surface and the electronic properties measured by photoemission of core levels.

Keywords: Alloying effect, Pt alloys, XPS binding energy, 1,3 butadiene hydrogenation

1. Introduction

Surface science investigations of the local order and electronic properties in surface of metal alloys in relation with their chemical reactivity are of major interest in order to develop a better understanding of catalysis by alloys. In that study we focused our attention on the intrinsic influence of some group VIII metals (nickel, cobalt, iron) on the surface properties of platinum. Indeed, by association of Pt with metal partners having a more or less d band filling, and being more or less electropositive, different physical and chemical properties can be expected. Moreover, the local order in surface (i.e. the surface segregation and the geometrical arrangement) can be different following the thermodynamic properties of each couple.

In the following are reported the hydrogenating properties of the (111) oriented $Pt_{80}X_{20}$ (X = Ni, Co, Fe) samples. We will describe first the local order in the very first layer, and then the hydrogenating properties of these samples for the 1,3 butadiene hydrogenation used as a test reaction.

2. Materials and experimental

All the considered samples present a quasi-complete monolayer of Pt in the very surface [1–4]. Moreover, the second layer is more or less depleted in Pt [2–4]. The layer by layer composition of these $Pt_{80}X_{20}$ (111) in the surface region are given in fig. 1.

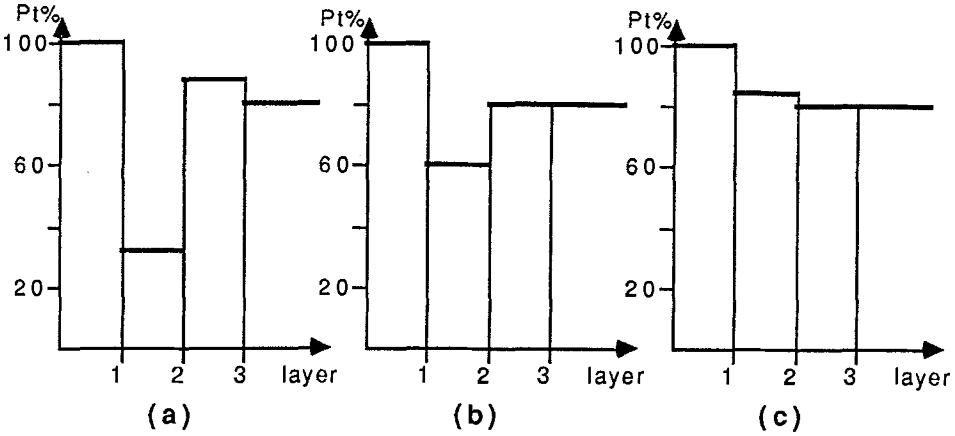

Fig. 1. Layer by composition of a) $Pt_{78}Ni_{22}$ (111) [4] b) $Pt_{80}Co_{20}$ (111) [2] c) $Pt_{80}Fe_{20}$ (111) [3].

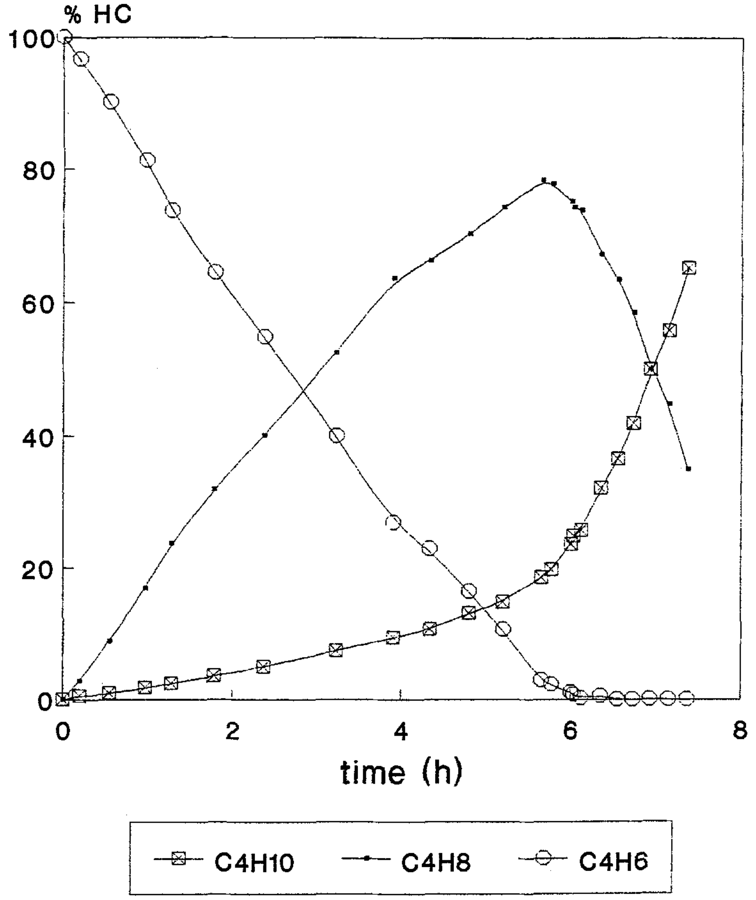

Fig. 2. Conversion vs. time for 1,3 butadiene hydrogenation on $Pt_{80}Fe_{20}$ (111). (300 K, $P_{H_2} = 300$ T, $P_{HC} = 3$, Torr, sample area 0.27 cm^2).

Moreover, one has to notice that the $Pt_{78}Ni_{22}$ and $P_{80}Co_{20}$ alloys exhibit a fcc bulk structure where Ni or Co atoms are randomly distributed, while the $Pt_{80}Fe_{20}$ alloy exhibits the ordered L12 type of structure (γ_3 phase) as checked by X-ray diffraction techniques. It is striking that such an ordered structure extends to the surface leading to a (2 × 2) LEED structure. Three fourth of the surface Pt atoms are bonded to two Pt and one Fe atoms in the sublayer. One fourth has only Pt atoms as first neighbours and are located slightly out of the mean position of the surface plane. It has to be added that some chemical substitutional disorder is present due to the deviation of the considered $Pt_{80}Fe_{20}$ alloy from the Pt_3Fe stoichiometry.

The samples can be transferred from the UHV chamber, in which cleaning and control of the alloy surface by LEED and Auguer electron spectroscopy are done, into a quartz reactor of 365 cm^3 volume separately pumped. The schematic representation of the experimental arrangement is given in ref. [5]. Catalytic reactions were performed at room temperature under static conditions.

Gas analysis of the reactants and products was carried out by mass spectrometry. After pumping off the reactive mixture, the samples were transferred to the UHV chamber in order to check the surfaces after reaction with the CMA Auger facilities.

Hydrogen (purity $> 99.9995\%$) and 1,3 butadiene (purity $> 99.5\%$, the main impurities being butenes) were used without further purification.

3. Results and discussion

In fig. 1 is given a typical diagram corresponding to a reaction run performed on the $Pt_{80}Fe_{20}$ (111) sample. A linear decrease of the 1,3 butadiene concentration is first observed, which agrees with a near zero order with respect to the hydrocarbon pressure. The main products are butenes (1-butene and 2-butenes) and at less extent butane. The selectivity $S_{\text{butenes}} = \text{butenes}/\text{butenes} + \text{butane}$ is nearly constant up to at least about 80% conversion of the diene. Then butenes are converted into butane. The turnover frequencies (TOF) (calculated assuming 1.506×10^{15} atoms.cm^{-2} in surface for the $Pt_{80}Fe_{20}$ (111) alloy and for pure Pt(111), and 1.57×10^{15} at.cm^{-2} for the considered PtCo and PtNi alloys), are given in table 1 for a 300 K reaction temperature under $P_{H_2} = 300$ Torr in large excess with respect to the diene ($P_{H_2}/P_{HC} = 10$). For the three considered Pt-X alloy samples, no significant changes in the X to Pt characteristic Auger peak intensity ratios were observed after reaction. This suggests that surface composition remain unaltered during the reaction. Only some carbon is left on the surface. Its determination, based on the $I_{237}(\text{Pt})/I_{275}(\text{C})$ Auger peak ratio and the method of calibration proposed by Biberian and Somorjai [8] (with some corrections taking into account the CMA versus RFA transmission differences with

Table 1
Activity and selectivity of pure Pt and PtNi, PtCo and PtFe alloys for 1,3 butadiene hydrogenation (300 K, $P_{H_2} = 300$ Torr, $P_{H_2}/P_{HC} = 10$)

In the third line is given the chemical shift of the core levels for both components as referred to the pure materials

Samples Experimental data	Pt(111)	$Pt_{78}Ni_{22}$ (111)	$Pt_{80}Co_{20}$ (111)	$Pt_{80}Fe_{20}$ (111)
TOF (s^{-1})	0.75	1.1	0.5	5.1
Selectivity				
at 20% conv.	0.68	0.75	0.77	0.91
at 50% conv.	0.58	0.73	0.71	0.89
E_b (*eV*)				
Pt 4f	0	+0.1	≈ 0	+0.2
Ni		−0.3		
Co 2p			+0.5	
Fe 3p				−1 [a]
		ref. [6]	ref. [2]	ref. [7]

[a] The Fe 3p core level data in ref. [7] has been taken equal to 52.7 eV [from J.C. Fuggle and N. Martensson, J. Electron Spectrosc. Relat. Phenom. 21 (1980) 275].

kinetic energy), leads to less than 0.4–0.5 of a monolayer of carbon (1 ML = 4×10^{15} C atoms per cm^2).

The association of Pt with Ni and Co generates a solid having a reactivity more or less comparable to that of pure Pt. The PtFe alloy is largely more active, and the most selective.

When considering only the chemical nature of the partner added to platinum, one can expect that iron could affect more deeply the electronic properties of Pt. Indeed, iron has the less filled d-band, and the lowest electronic affinity. However, by such considerations cobalt would have an intermediate influence between Ni and Fe. This does not fit with the experimental observation (table 1). However, when regarding the Pt4f core level chemical shifts measured by XPS photoemission a correlation can be attempted between the chemical reactivity and the Pt4f chemical shift: the larger is the shift upwards, the higher is the activity of the solid for 1,3 butadiene hydrogenation. Nevertheless, it is obvious that the Pt4f core level shifts are small, and nearly in the limit of the precision of the XPS spectroscopy. However, when considering the effect on the second metal, the chemical shifts measured on the 2p, 3p core levels of Ni, Co or Fe are largely more relevant and out of the uncertainty; the shift downwards is very large for Fe, smaller for Ni and is opposite for Co. Assuming a reciprocal mutual influence the Pt perturbation would follow the sequence PtFe > PtNi > Pt > PtCo which fits well the observed sequence for the hydrogenation activity. These shifts are the consequence of the intermetalling bonding energy which is largely stronger for PtFe than for PtCo or PtNi [10]. Moreover, some additional energy has to be taken into account for the $Pt_{80}Fe_{20}$ alloy due to the ordering.

In the previous discussion we have only considered the mean electronic effect, i.e. the effect induced by alloying in the bulk of the materials. Such considerations should have to be discussed for the surface atoms, which are in contact with the reactive mixture during the course of a hydrogenation reaction. Unfortunately, only few data are up to now available. On Pt(111), the $4f_{7/2}$ core level energy corresponding to surface atoms with 9 nearest neighbours has been measured at 70.65 eV, i.e. at an energy 0.35 eV lower than for highly coordinated bulk Pt atoms [9]. On $Pt_{80}Fe_{20}$ (111) recent experiments indicate that two kinds of Pt atoms are present in surface with binding energies equal to 70.75 eV, and 70.60 eV; they would correspond respectively to Pt surface atoms coordinated to two Pt and one Fe atoms in the sublayer (three fourth of the surface Pt atoms) and to three Pt in the second layer (one fourth of the surface atoms) [7]. As in the bulk a slight shift upwards is observed for the Pt surface atoms in contact with some Fe atoms.

When considering only the first nearest neighbours located in the sublayer of the Pt surface atoms, it is surprising that few Fe atoms (20–25% in the second layer) affect more notably the properties of the outer Pt atoms than more Co (38% in the sublayer) and even more Ni (70% in the second layer). It would indicate that the electronic interaction between the surface Pt atoms and the atoms belonging to the third in depth plane is important and has a noticeable influence on the physico-chemical properties of the surface sites. Such an interaction would be less important for alloys showing an oscillatory composition (case of Pt-Ni (111) alloys) than when a monotonous decrease of the Pt surface segregation exists (case of the $Pt_{80}Fe_{20}$ (111) sample).

Moreover, the ordered L12 bulk structure of the PtFe sample induces a special geometrical design of the surface via the slight buckling outwards of one fourth of the Pt surface atoms. Such a phenomenon could be responsible to a geometrical effect inducing some changes of the 1,3 butadiene bonding which would have a more or less pronounced di-σ or π character; it is well known that such changes are accompanied by modifications of hydrogenating activity and selectivity [11,12].

In conclusion, the catalytic behaviour of Pt with respect to butadiene hydrogenation is modified by alloying Pt with Ni, Co and Fe. The effect is the more pronounced for Fe. No simple explanation may be invoked, but some trends can be drawn:

- The modifications of the electronic properties evidenced by the core level energy shifts of the two components which are the consequence of intermetallic bonding energies. More relevant would be a knowledge of these shifts for the atoms present in the first layer; nevertheless, some first results indicate that the shifts in surface follow the shifts in the bulk [7,13].

- The monotonous or oscillatory segregation for which the influence of the interaction with the third in depth plane is respectively more or less important.
- The geometrical arrangement in surface which may modify the adsorption mode of the reactants.

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