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1,3-butadiene hydrogenation on $Pd_{50}Cu_{50}$ single crystals

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The catalytic properties of (111) and (110) $Pd_{50}Cu_{50}$ single-crystal surfaces have been tested for the 1,3-butadiene hydrogenation reaction, and compared to those of pure Pd having the same surface orientations. The $Pd_{50}Cu_{50}$(111) single crystal has the highest activity; it is also more effective than the corresponding pure Pd face. The activity of the $Pd_{50}Cu_{50}$(110) is less; nevertheless, it is practically as effective as the Pd(110) crystal, which is itself more effective than the (111) oriented Pd sample. The results are discussed in terms of both geometric and electronic effects. They are associated on one side to the dilution by the inactive Cu surface atoms, and on the other side to the electronic interaction between the outer Pd surface atoms and the surrounding Cu atoms.

Keywords: palladium, copper, alloys, single crystals, 1,3-butadiene

1. Introduction

The influence of the surface structure of a metal (coordination number and geometric arrangement of surface atoms) on its catalytic properties is crucial. In the case of pure metals the reactivities are generally different especially for reactions involving dissociation or bond breaking, but also in the case of hydrogenation reactions, as observed for example for Pd(111) and Pd(110) single crystals employed for the hydrogen / butadiene reaction [1].

In the case of alloys, segregation phenomena and, of course, their dependence on the crystal orientation should also be taken into account. Employing a mixed-metal system instead of the single-metal counterparts for a given reaction can enhance activity and / or selectivity. The phenomena controlling the performances for heterogeneous catalysis of these systems are understood either in terms of the geometric “ensemble effect” (number of surface atoms of a given element needed for the catalytic process to occur) or of the “ligand effect” (electronic modifications induced by the components of the system); moreover, some “bi-site effect” (both components play a specific role with respect to the partners of the catalytic reaction) can also occur. As a consequence, the concentration and arrangement of both components at the extreme surface, but also those of the sublayers which may electronically influence the outer layer, need to be known in order to understand the catalytic behaviour of such bimetallic alloys.

The use of well defined samples which can be probed by a variety of surface science techniques makes a better understanding of the catalytic mechanisms possible. Precious metals, which are considered the best catalysts for many reactions, are generally incorporated into bimetallic systems. In the following paper we will present results obtained on the surface of Pd–Cu single crystal alloys in the close-packed (111) and in the more open (110) orientations. The test reaction chosen is the hydrogenation of butadiene, a reaction for which Pd is the most commonly used catalyst. The surface characterisation is done by Auger electron spectroscopy (AES) and low electron energy diffraction (LEED).

2. Experimental

The Pd–Cu single crystal was obtained from Cristal-Tec, in the shape of a bar of about 1 cm diameter. The samples were cut by spark erosion along the desired (111) and (110) orientations. The sample surfaces were 0.51 and 1 cm^2 respectively. They were polished with the use of diamond paste to a grain of less than 1 μm, before treatment in the UHV conditions.

Clean surfaces were obtained by repeated cycles of Ar^+ ion bombardment (3.5 keV energy) and heating at about 870 K in an UHV system (base pressure of 2×10^{-10} mbar). LEED and AES facilities are also available in order to control in situ the surface before and after reaction.

The experimental setting has been fully described elsewhere [2]. The low-volume reactor (84 cm^3) operates in the static mode; it has been slightly modified in order to make sampling for chromatographic analysis possible. The advancement of the reaction is first followed by means of a mass spectrometer located in the UHV chamber communicating through a leak valve with the reactor. In a second experiment, the reaction gases were introduced, through a valve, into a smaller volume (< 3 cm^3) in which a nipple was adjusted. A gas sample could thus be taken several times during a reaction run by means of a syringe (1 ml) through the nipple and then analysed by gas phase chromatography. Care was taken in order to limit the number of samplings so that the reaction rate was not perturbed by the modification of the partial pressures and by the possible introduction of some air through the nipple.

3. Results

In table 1 are reported the AES results obtained for the two samples after cleaning (Ar^+ ion bombardment and annealing at 870 K). No other elements apart from Pd and Cu were detected. The interference of the Pd_{279} and C_{272} peaks compel us to use the $(Pd_{279} + C_{272})/Pd_{330}$ ratio in order to evaluate the surface state. This ratio is found to be 0.25 for pure Pd; we can therefore assume that the sample surfaces are free of carbon.

A (1 × 1) LEED pattern was observed for the (111) sample following sputtering and annealing. In the case of the (110) sample the spots observed in the LEED (1 × 1) pattern were generally not very sharp. However, in certain cases depending on the sample preparation, extra spots in 1/2 along the $[1\bar{1}0]$ direction were visible. The difficulty in obtaining sharp LEED patterns is probably due to the relatively disordered surfaces resulting from the low order–disorder transition temperature along with segregation effects [3].

The hydrogenation reaction was performed at $T = 300$ K, under a total pressure of about 25 mbar; the $P_{H_2}/P_{C_4H_6}$ ratio was 5. The evolution of the butadiene, butenes and butane pressures, monitored by mass spectrometry versus reaction time, are plotted in figures 1a and 2a, in the cases of PdCu (110) and (111) respectively.

For both orientations the conversion of butadiene to butenes is highly selective up to the total conversion of the butadiene. The linear decrease of the butadiene pressure versus time agrees with a zero order with respect to this reagent, which is generally observed [4]. The butadiene hydrogenation reaction is considered to be a zero-order reaction respective to the hydrocarbon concentration and a positive-order reaction (order about 1) respective to hydrogen concentration The butadiene hydrogenation is more rapid in the case of the (111) sample than in the case of the (110). We should note here that the results presented in figures 1 and 2 are not corrected for the crystal surfaces. In other words, the butadiene conversion to butenes is accomplished in ~ 5000 s for the (110) sample having a 1 cm^2 surface and in ~ 1000 s for the (111) one having a 0.51 cm^2 surface. The second reaction (butenes to butane) progresses at a lower rate, which decreases as the reaction goes on. A 70% conversion to butane is thus accomplished in ~ 30000 s for the (110) sample and in ~ 9000 s for the (111).

Using mass spectrometry it is not possible to separate the butene isomers from each other. The experiments involving sampling and analysis by gas phase chromatography allow us to follow the evolution of butene isomers during reactions. The butadiene, 1-butene, cis-2-butene, trans-2-butene and butane percentages monitored by the chromatograph are plotted against the reaction time in figures 1b and 2b respectively for PdCu (110) and (111) (the $\sum C_4H_8$ curve corresponds to the sum of the 1-butene, cis-2-butene and trans-2-butene contributions). One can distinguish two distinct phases during the hydrogenation reaction. During the first one, 1-butene and trans-2-butene are mainly formed. Either just before the complete conversion of butadiene or at the beginning of butenes hydrogenation, a rapid isomerisation reaction is evidenced:

$$\text{1-butene} \rightarrow \text{trans-2-butene} + \text{cis-2-butene}$$

The second phase corresponds to the hydrogenation of butenes. The 1-butene hydrogenation appears to proceed faster than that of 2-butenes, but competes with the isomerisation reaction into 2-butenes. Such phenomena are commonly encountered in the case of pure Pd [5,6]. The combination of such a competition with different hydrogenation rates for 1- and 2-butenes together with the significant decrease of the H_2 pressure in the course of the run explains the non-linearity of the curves reported in figures 1a and 2a after the total conversion of 1,3-butadiene.

To summarise, after the complete conversion of butadiene, the 1-butene is very rapidly isomerized to cis-butene or trans-butene or converted to butane. Afterwards, in excess of hydrogen, the complete hydrogenation into butane occurs.

In table 1 are also reported the catalytic activities (calculated for $P_{H_2} = 13.33$ mbar and with the assumption of a first-order reaction for H_2 as generally found [4]) obtained on the two different PdCu single crystals

Table 1
AES peak to peak ratios, activities (extrapolated for 13.33 mbar for the hydrogen pressure) and Pd surface content (from LEIS data [7,10]) obtained for the samples studied

	PdCu(110)	PdCu(111)	Pd(110)	Pd(111)
AES				
$(Pd_{279}+C_{272})/Pd_{330}$	0.262	0.238	~ 0.25	
Cu_{60}/Pd_{330}	2.3	1.02		
activity (10^{15} molecules cm^{-2} s^{-1})	1.36	11.31	2.14	0.43
n^{Pd} (10^{15} atoms/cm^2)	0.3	0.75	0.94	1.54

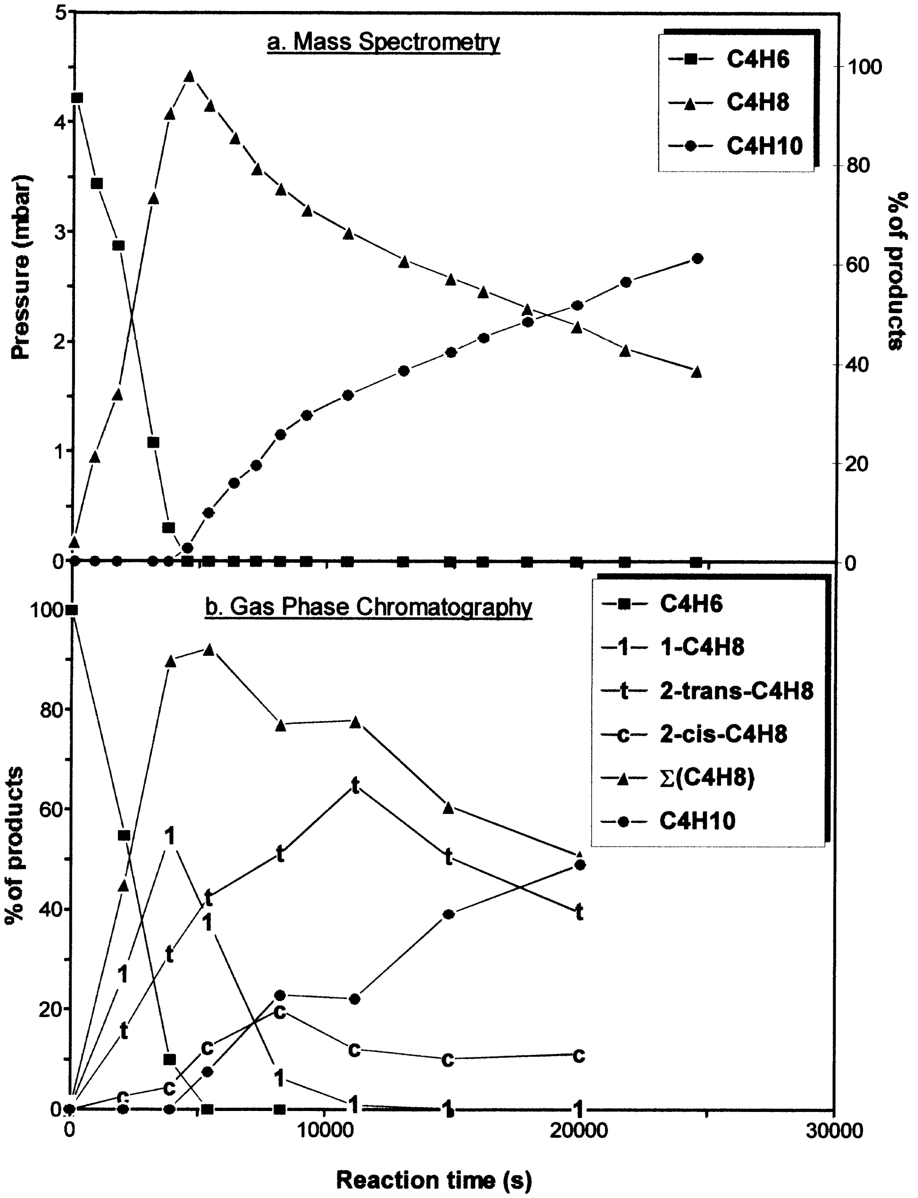

Figure 1. Butadiene hydrogenation reaction catalysed by a PdCu(110) single crystal (surface = 1 cm^2): The butadiene, butenes and butane concentrations versus the reaction time are followed by (a) mass spectrometry and (b) gas phase chromatography.

examined in this study. They are compared with the results previously obtained for pure Pd samples having the same surface orientations [1]. One has to note that, in the case of pure Pd single crystals, the H_2 pressure was maintained at 6.67 mbar in order to avoid the bulk hydride formation which provokes the destruction of the monocrystalline state of the crystals.

After each reaction, the samples were analysed in situ by AES. The presence of carbon is the only significant change stated.

4. Discussion

The activity of the PdCu(111) crystal is enhanced compared to that of the Pd(111), and the activity of the PdCu(110) is practically at the same level as that of the Pd(110). This is remarkable, if one supposes that the active metal is Pd. Indeed, due to dilution by the inactive Cu surface atoms there are fewer active sites in the case of the alloys than for pure Pd. Consequently, one has to consider ligand effects to explain the activity enhancement. XPS experiments on PdCu alloys have evidenced some shifts of core and valence levels, accompanied by a lowering of the asymmetry of the Pd 3d XPS peaks as compared to pure Pd [7–9]. This is characteristic of fewer empty states in the Pd d band, in PdCu as compared to pure Pd, probably owing to an interaction via bond formation between the almost full valence "sd" band of Pd and the resonant "dsp" band of Cu near the Fermi level.

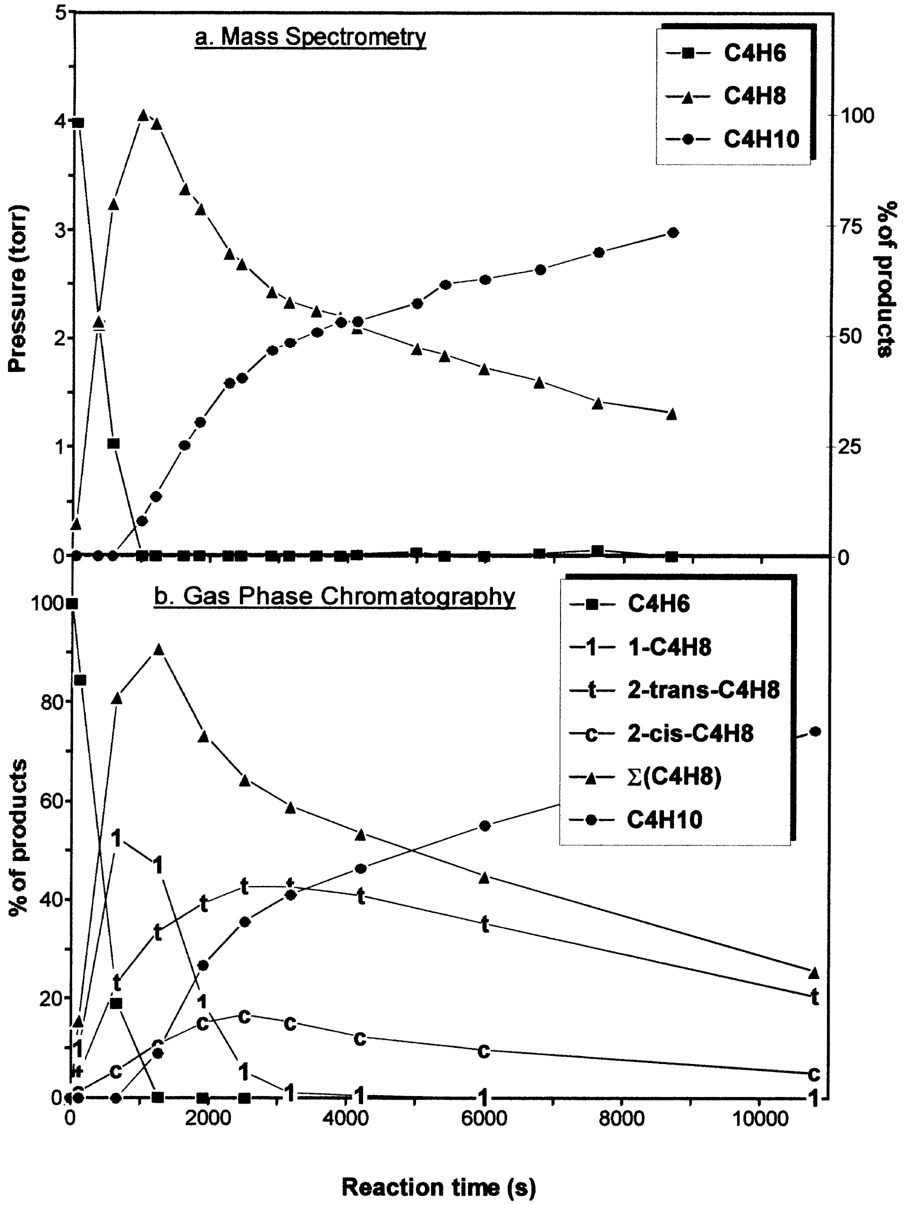

Figure 2. Butadiene hydrogenation reaction catalysed by a PdCu(111) single crystal (surface = 0.51 cm^2): the butadiene, butenes and butane concentrations versus the reaction time are followed by (a) mass spectrometry and (b) gas phase chromatography.

This is also manifested through the decrease of the heat of adsorption of CO and NO on Pd in the alloy with respect to pure Pd [7,10]

These changes in the electronic and chemisorptive properties will reflect to the adsorption and/or mobility of the reactants and the reaction intermediates (hydrocarbons and hydrogen). It was shown that hydrogen adsorbed on PdCu [11] presents a weaker interaction with the alloy surfaces compared to pure metal surfaces. In other words hydrogen is more mobile in the case of alloy surfaces. The same arguments can be retained for adsorbed butadiene. Indeed, recent studies have suggested that the C=C–C=C conjugation is slightly less affected for PdCu(111) than on Pd(111) which indicates a weaker coupling with the surface [12]. In addition to the mobility of the butadiene molecules, the change induced in its chemisorption state can also modify the intrinsic probability for H insertion in it. This is, indeed, a step of major importance when activity is under consideration.

In any case, butadiene is more strongly bonded to the surface than butene. This explains the good selectivity of Pd alloys for this reaction (butene will desorbe as long as butadiene is present in the reaction gas mixture).

Surprisingly, the activity of the PdCu(110) is lower than that of the PdCu(111). Indeed, the more open faces of Pt, Pd, Ni generally show a greater activity (about an order of magnitude) than the close-packed ones. Many reasons may be invoked to explain this discrepancy.

First of all, the Cu_{60}/Pd_{330} ratio measured in the AES spectra for the two alloy samples clearly indicates a lower Pd content (element considered to be the active one for the studied reaction) in the surface region of the (110) oriented sample. This is in agreement with previous LEIS measurements, from which the magnitude of surface segregation has been determined [7,10]. In the case of the (111) crystal a slight segregation of copper leading to a surface composition of $Pd_{45}Cu_{55}$ was observed. The copper segregation is more pronounced on the (110) oriented alloy, and leads to a surface composition of the outer rows corresponding to $Pd_{30}Cu_{70.}$

The activity of the PdCu(111) crystal is eight times as high as that of PdCu(110). However, there are only twice as many Pd atoms at the first monolayer of PdCu(111) than that of PdCu(110). A number of hypotheses could be advanced in order to explain this result, in addition to the ones exposed above, concerning mobility and/or interaction of the reactants and intermediaries with the surfaces. It has been suggested that the active site with respect to the butadiene molecule is a Pd pair [12–15]. Such a site (formed by two adjacent Pd surface atoms with adsorption of the butadiene in a di-π configuration) has been proposed for Pd from a theoretical approach [14]. This is in agreement with recent XANES analysis on pure Pd [12,15] but also on PdCu(111) [12]. The Cu/Pd atomic ratio of the topmost layer determined by LEIS is higher on the (110) face compared to the (111) one, 0.7/0.3 instead of 0.55/0.45, and thus the probability of having Pd–Pd pairs would be lower than for PdCu(111).

Finally, the tendency to form of a $PdCu_3$ $L1_2$ ordered phase [3,16] on the (110) sample could be invoked. Indeed, the stoichiometry of such a phase is very near that of the outer surface composition determined from LEIS experiments. Moreover, the high value of the AES ratio $Cu_{60}/Pd_{330} = 2.3$ indicates that the Cu enrichment extends in depth to some atomic subsurface layers. In such an ordered arrangement, the surface would be, as shown in figure 3, a combination of pure Cu terraces (a), inactive with respect to the considered reaction and mixed PdCu planes (b) having the tendency to generate an ordered arrangement in which Pd and Cu atoms alternate. This agrees with the observation of extra spots in some of the LEED patterns. The loss of activity could be thus associated to the dilution of Pd by Cu and/or to the rearrangement of Pd and Cu in the PdCu terraces.

5. Conclusion

The PdCu(111) and (110) alloys present the same trends concerning their catalytic properties towards the selective hydrogenation of 1,3-butadiene. In comparison with pure Pd they exhibit the following performances:

– The selectivity to butenes remains equal to 1 up to 100 % conversion.

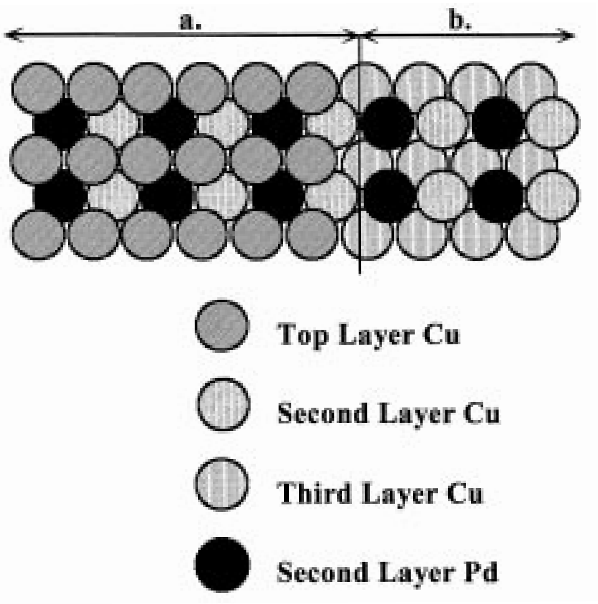

Figure 3. The possible surface arrangement for the ordered $L1_2$ $PdCu_3$ phase: (a) Cu terminated, (b) PdCu terminated.

– The behaviour with respect to the formation, isomerisation and/or hydrogenation of butene isomers throughout the reaction is very similar.

– The activity is enhanced even though the total number of Pd sites is lower, due to a "positive" electronic ligand influence of Cu surrounding atoms on the active Pd surface atoms.

Moreover, the fact that the activity of the PdCu(111) crystal is eight times higher than that of PdCu(110) while there are only twice as many Pd atoms in the outer layer can be tentatively explained by the tendency to form a $PdCu_3$ ordered phase in the surface region, in a scheme in which the active site would be constituted of two adjacent Pd atoms.

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