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NOTES

$Pt_{0.5}Ni_{0.5}(111)$ Single-Crystal Alloy: Activity and Selectivity for Hydrogenation of 1,3-Butadiene as Compared to Pure Pt(111)

Pt–Ni alloy single crystals have been used to investigate the modifications of chemical and catalytic properties of these transition metals induced by alloying. The surface of such samples can be well characterized by using physical techniques such as electron, ion, and photon spectroscopies.

Whatever the nominal bulk composition the clean surfaces equilibrated by heating at 1100 K are enriched with platinum, as shown by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and ion scattering spectroscopy (ISS) (*1, 2*). Such Pt enrichment has already been reported on polycrystalline Pt–Ni alloys (*3*). On a $Pt_{0.5}Ni_{0.5}(111)$ sample and for crystals of larger platinum bulk content, a quasi-complete platinum surface layer (less than 2–4 at.% nickel) is present (*1, 2*).

With respect to the pure components, a decrease of chemisorption strengths for H_2, C_6H_6, C_2H_4, and CO is always observed after alloying (*4–6*). A more pronounced effect is noted on the $Pt_{0.5}Ni_{0.5}(111)$ sample used in the present work. In the same way, the catalytic activities for benzene hydrogenation and benzene–deuterium exchange are lowered by alloying (*6, 7*).

For the $Pt_{0.5}Ni_{0.5}(111)$ sample which exhibits a platinum outer layer with novel chemical properties with respect to pure platinum, specific behavior in selective hydrogenation can be expected. Indeed, the activation of reactants and intermediate products is modified and this directly influences the reaction rates, and therefore the selectivity.

This work deals with the comparison of pure Pt(111) and $Pt_{0.5}Ni_{0.5}(111)$ alloy in the selective hydrogenation of 1,3-butadiene, a reaction of practical importance for the purification of C_4 olefin cuts containing residual butadiene.

The bulk concentration of the alloy is 50 at.% in each component. It exhibits the fcc structure characteristic of the α-phase solid solution (*8*). The samples are in the shape of thin slabs of about 1 cm diameter. After mechanical polishing up to 1 μm, the surface recrystallization was achieved simply by heating to 1400 K under high vacuum. The surface is within 1° of the (111) plane; it exhibits after cleaning a well-contrasted (1×1) LEED pattern with sharp diffraction spots. The same procedure has been followed to condition the pure Pt(111).

The sample can be transferred from the ultrahigh vacuum chamber, in which cleaning and control (by LEED and Auger electron spectroscopy using a two-grid retarding field analyzer) are performed, into a quartz reactor of about 200 cm^3 volume, in which catalytic reactions are followed. Gas analysis is carried out by mass spectrometry.

Hydrogen (purity >99.9995%) and butadiene (purity >99.5%, the main impurities being butenes) were used without further purification. The reaction was performed at room temperature under static conditions with 4.5 Torr of butadiene and 660 Torr of hydrogen. Results are shown in Fig. 1. The time scale has been corrected in order to take into account the surface area difference of the two crystals; the reported curves correspond to samples of 1 cm^2 sur-

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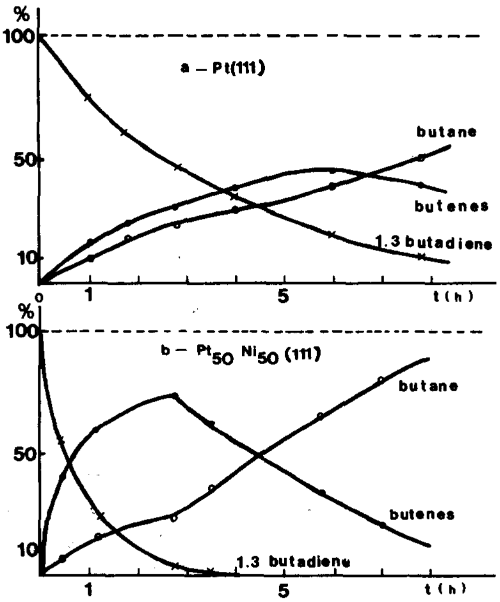

FIG. 1. Conversion versus time for butadiene hydrogenation on: (a) Pt(111), (b) $Pt_{0.5}Ni_{0.5}(111)$. P_{HC} = 4.5 Torr; P_{H_2} = 660 Torr; 300 K.

face area. The main features are a higher activity and a better selectivity toward butenes on the alloy sample as compared to pure platinum. The initial activity, measured from the decrease of the butadiene partial pressure, is about 3–4 times larger on the Pt–Ni catalyst (Table 1).

The reaction leads to butenes and butane. The selectivity toward butenes is significantly higher on the alloy single crystal and remains better than 80%, even at high conversion. Moreover, when the hydrogen/hydrocarbon ratio is decreased, the selectivity on the alloy sample is increased to such an extent that the amount of butane is not accurately measured under our experimental conditions.

The nature of butenes cannot be precisely determined with our quadrupole gas analyzer. In order to determine the relative quantities of butene-1, *cis*-butene-2, and *trans*-butene-2, a sample of the reaction mixture at about 95% conversion of butadiene, after reaction on the alloy, has been analyzed by gas chromatography. Equivalent amounts of butene-1 and *trans*-butene-2 are detected; the quantity of *cis*-butene-2 is much smaller.

The Auger spectra recorded on the alloy sample before reaction (curve *a*) and after one reaction run (curve *b*) are shown in Fig. 2. After butadiene hydrogenation, a significant increase of the Auger peaks at 150 and 272 eV is seen. They are respectively associated with the presence of sulfur, and carbon and (or) hydrocarbon species at the surface. According to the calibration of Berthier *et al.* (*9*), the sulfur coverage, expressed as the number of sulfur atoms per metallic surface atom, is about 4%. For carbon, the comparison of our data with those reported for C on Pt, measured with a retarding field analyzer and a coaxial incident beam (*10*), shows that the carbon coverage is about half a monolayer (one monolayer corresponding to about 2.5 C per Pt surface atom). This value is likely to be an overestimate since the near grazing incidence used in our experiment favors the intensity of the carbon outer layer with respect to that of

TABLE 1

Comparison of the Activity and Selectivity for Butadiene Hydrogenation ($P_{C_4H_6}$ = 4.5 Torr; P_{H_2} = 660 Torr; 300 K) on Pt(111) and $Pt_{0.5}Ni_{0.5}(111)$

Samples	Initial activity (turnover frequency, s^{-1})	Selectivity $S = \frac{\text{butenes}}{\text{butenes + butane}}$	
		at 50% conversion	at 80% conversion
Pt(111)	~1.5	58%	54%
$Pt_{0.5}Ni_{0.5}(111)$	~5	86%	80%

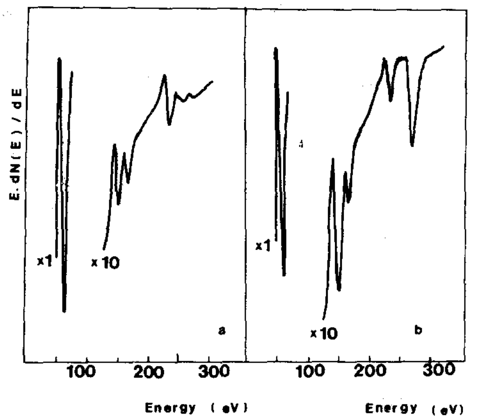

FIG. 2. Auger electron spectra of $Pt_{0.5}Ni_{0.5}(111)$: (a) clean sample, (b) after butadiene hydrogenation (primary energy: 2.5 keV; near grazing incidence).

the metal beneath. This carbon deposit is quickly eliminated by heating for a few minutes at 800°C, probably by desorption of carbon residues. The resulting surface is still active for butadiene hydrogenation. After three or four successive runs, the selectivity toward butenes is enhanced. This is probably related to the presence of sulfur and (or) carbon at the surface, which would favor partial hydrogenation. The activity is not sharply decreased.

These experimental results clearly show the changed behavior of the quasi-complete outer layer present on the $Pt_{0.5}$–$Ni_{0.5}(111)$ sample with respect to pure Pt(111). Indeed, the $Pt_{0.5}Ni_{0.5}(111)$ alloy sample, which shows very weakened chemisorptive properties compared to Pt(111) (*4*, *5*), leads also to more selective hydrogenation of butadiene toward butenes. The activity is even higher than that measured on Pt.

This difference in the selectivity toward partial hydrogenation of dienes between $Pt_{0.5}Ni_{0.5}(111)$ and Pt(111) cannot be explained by the presence of S impurity on the surface of this alloy sample, sulfur being an additive which is known to increase the selectivity for such reactions toward olefinic hydrocarbons, since it is also detected, in a quite similar amount, on Pt(111).

Two reasons may be invoked to explain this enhanced selectivity: (i) the competition of adsorption between butadiene and butenes may be displaced toward the diene, and (ii) the rate constants would be changed, due to a different activation of the adsorbed molecules.

Competitive adsorption probably favors butadiene with respect to the olefinic compounds. Indeed, in the presence of a large excess of ethylene (C_2H_4/butadiene = 10), butadiene is still preferentially hydrogenated to butene. However, an effect on the intrinsic rate constants for both diene and olefin hydrogenation cannot be ruled out.

A priori the different behavior of the alloy sample with respect to pure platinum seems surprising, since on the alloy sample an almost complete platinum outer layer is formed. However, either the different nickel content in the sublayers may differently influence the surface metallic atoms or the underlying metal can cause an epitaxial strain in the outer layer, which modifies the physical and chemical properties of the platinum surface atoms. Indeed, the observation of a strongly contrasted (1 × 1) LEED pattern suggests that the surface atoms are in registry with the bulk lattice, which is contracted by 4.3% for the alloy with respect to pure platinum (*8*).

However, whatever the predominant effect, the Ni content in the sublayers or epitaxial strains, a new catalyst has been formed which exhibits specific catalytic properties, especially for the selective hydrogenation of butadiene. Such results can be usefully compared to those of Sachtler *et al.* on Pt/Au (100) monolayers (*11*), on which an important increase of activity towards cyclohexene dehydrogenation has been observed (*12*).

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