

Determination of the Surface Composition of Pd-Ni/Al₂O₃ Catalysts by Chemisorption Methods

The activity of bimetallic systems is determined first of all by the surface and not by the bulk composition of the metallic phase. Changes of the surface composition in relation to the bulk one are mainly connected with the phenomenon of surface segregation (1, 2).

In the present paper an attempt has been made to determine the surface composition of Pd-Ni/Al₂O₃ system. Palladium and nickel form an alloy—a solid solution within the whole range of concentrations (3). Both nickel and palladium reveal similar surface reactivities at room temperature in relation to such adsorbates as H₂, O₂, CO (4). As it results from the present paper different reactivities of the oxidized surfaces of nickel and palladium toward hydrogen, at room temperature, may be the basis for the method of determining the surface composition of Pd-Ni/Al₂O₃ catalysts.

The subjects of the investigation were 2 and 5% Pd-Ni/Al₂O₃ catalysts prepared as described in Ref. (5). Measurements of hydrogen and oxygen adsorption and H_T-O_T titrations were carried out in the apparatus for pulsed gas chromatography investigations (6) (volume of capillary—0.56 cm³, volume velocity of a carrier gas—argon, 50 cm³/min).

The temperature-programmed reduction process (TPR) of the surface oxidized catalysts was carried out in the same apparatus under the conditions described in Ref. (5).

On the basis of the preliminary investigations of the hydrogen and Pd-Ni/Al₂O₃ interactions (under conditions of the pulsed method) no effect of hydrogen absorption in the metallic phase has been found. Moreover, it results from Ref. (7) that the addi-

tion of more than 30 wt% of Ni to Pd prevents hydrogen from being dissolved in Pd-Ni alloy, which was confirmed in our previous paper (5) for the systems under investigation indirectly it indicates the presence of an alloy in Pd-Ni/Al₂O₃ catalysts.

Results of hydrogen (H_c) and oxygen (O_c) chemisorption as well as H_T-O_T titrations for 2% Pd-Ni/Al₂O₃ catalysts, as a function of bulk composition, are presented in Fig. 1.

The values of the first titration O_{T1} (the amount of the oxygen uptaken in the titration reaction of the hydrogen-covered surface H_c) and the values of oxygen chemisorption O_c for nickel and nickel-rich systems are practically equal. It suggests that hydrogen primarily adsorbed on the surface of nickel does not react with oxygen forming water but is displaced to the gas phase by oxygen being adsorbed. The values of the successive titrations of O_T and H_T for the same catalysts are practically equal to zero under the conditions of the method used. It indicates that the oxidized surface of nickel at room temperature does not react with gaseous hydrogen.

However, the statement about nonreactivity of the oxidized surface of nickel in relation to hydrogen at room temperature may prove controversial. Benninghoven *et al.* (8) and Borcskov *et al.* (9) claim that when the coverage of the nickel surface with oxygen is less than monolayer, it reacts with hydrogen thus forming hydroxyl groups, nonreactive at room temperature. Benninghoven *et al.* (8) also suggest that oxygen displaces hydrogen previously adsorbed on the nickel surface to the gaseous phase but does not react with it. They no-

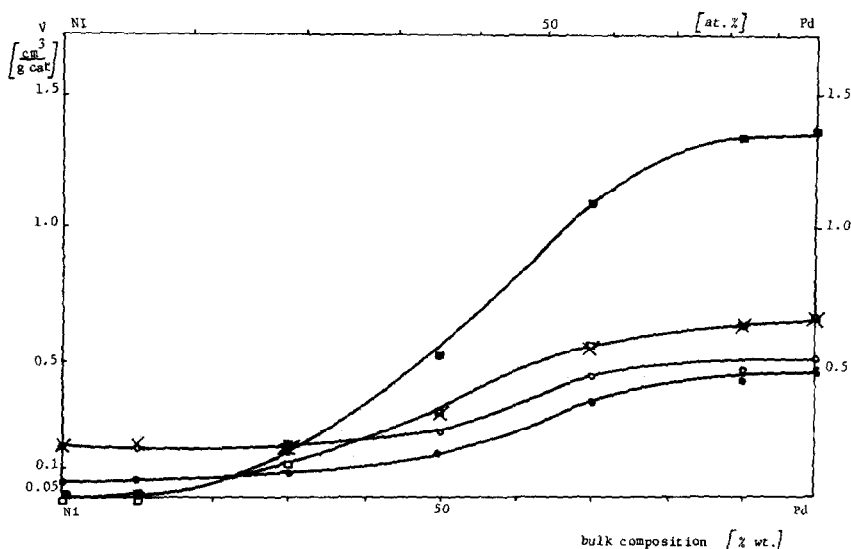


FIG. 1. Results of hydrogen (H_c) and oxygen (O_c) chemisorptions and hydrogen (H_T) and oxygen (O_T) titrations as a function of bulk composition of 2% Pd-Ni/ Al_2O_3 catalysts. ■, H_T ; □, O_T ; ●, H_c ; ○, O_c ; ×, O_{T1} .

ticed various stages of oxidation of the nickel surface depending on the time of exposure to oxygen which is revealed by different reactivities of the oxidized surface in relation to hydrogen.

In order to determine the reactivities of the oxidized surfaces of Pd-Ni/ Al_2O_3 catalysts at room temperature TPR with hydrogen from gaseous phase (the mixture of 10 vol% H_2 -90 vol% Ar) has been applied.

The results of the surface TPR for 5% Pd-Ni/ Al_2O_3 catalysts for different compositions of the metallic phase are shown in Fig. 2.

The maximum rate of hydrogen uptake for Ni/ Al_2O_3 , after its previous pulse surface oxidation in a stream of neutral gas argon, occurs at about 450 K (curve 1). For the same catalysts curve "a" in Fig. 2 represents TPR after the previous pulse surface oxidation in a stream of the reducing mixture at room temperature. The comparison of the curves "a" and 1 shows that irrespective of the way of oxidation, the sample is covered with a quantitatively comparable layer of oxygen. The increase of the palladium content leads to the decrease of the area under the curves with a

simultaneous shift of the maximum of hydrogen uptake toward the lower temperatures. For palladium-rich systems (curves 5 and 6) only the peaks responsible for hydrogen desorption, following its absorption at room temperature, can be seen.

Assuming that the titration reactions H_T - O_T at room temperature take place only on the palladium surface atoms, the curves of titration in Fig. 1 represent a quantitative share of palladium atoms on the surface of the metallic phase. On the other hand, the contribution of the surface atoms of nickel can be evaluated by the determination of the area under the curves 1-4 in Fig. 2. Thus we assume that there is no activation of the surface nickel atoms by palladium in the titration reactions H_T , O_T . Low results of titration H_T in case of catalysts containing up to 30 wt% of Pd in the metallic phase (Fig. 1) as well as the occurrence of reduction effects even for palladium-rich systems (70 wt% of Pd—curve 4 in Fig. 2) suggest that the role of the palladium activation effect is not too important. Otherwise a small amount of palladium on the surface would lead to a considerable surface reduction of the catalysts already at room temperature.

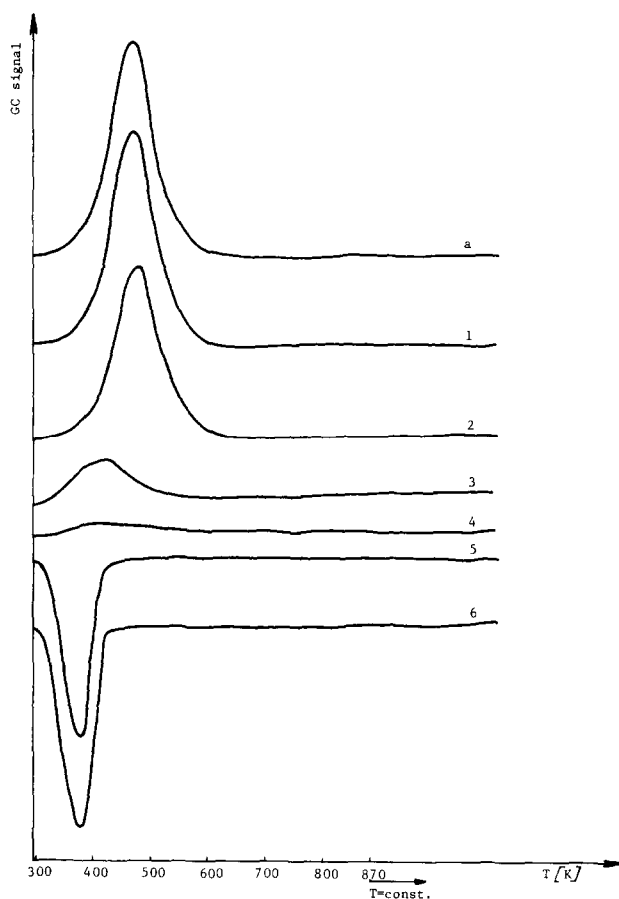


FIG. 2. TPR results of surface-oxidized 5% Pd-Ni/Al₂O₃ catalysts in a stream of argon (curves 1-6) and in a stream of reduction mixture (hydrogen-argon) (curve a). (a) 100% Ni, (1) 100% Ni, (2) 90% Ni-10% Pd, (3) 50% Ni-50% Pd, (4) 30% Ni-70% Pd, (5) 10% Ni-90% Pd, (6) 100% Pd.

However, it has been shown by Mössbauer spectroscopy (10-12), that the reducibility of Fe is increased by Pd such that Fe participates in H_T-O_T titrations at room temperature. Although Ni is more reducible than Fe, it can be assumed that Pd does not change substantially surface properties of Ni in H_T-O_T titrations. The increase in the degree of reduction of nickel in Pd-Ni system does not necessarily suggest changes in reactivity of Ni surface atoms in H_T-O_T titrations. Thus we assume that the behavior of Ni-Pd is different from that of Fe-Pd.

On the basis of the results of the titrations H_T-O_T (Fig. 1) and TPR (Fig. 2) the surface composition (Fig. 3) of 2% (curves 3 and 4) and 5% (curves 1 and 2) Pd-Ni/

Al₂O₃ catalysts has been determined as a function of the bulk composition of the metallic phase. In the case of 5% Pd-Ni/Al₂O₃ systems their surface, within the whole range of concentrations of palladium and nickel, is enriched in palladium. The comparison of the heat of sublimation for palladium—376 kJ/mole and nickel—430 kJ/mole (13) indicates the possibility of segregation of palladium on the surface of Pd-Ni alloy (14). A similar composition of the equilibrium Pd-Ni films was obtained by Moss *et al.* (14, 15) who used Auger electron spectroscopy. The differences between the surface compositions of 2 and 5% catalysts result probably from the stronger (for 2%) metal-carrier interactions and also

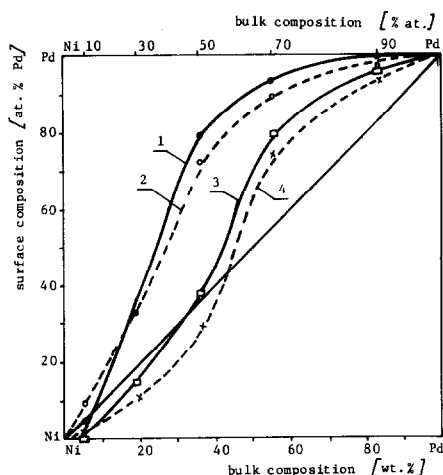


Fig. 3. Surface composition of 2% (curves 1, 2) and 5% (curves 3, 4) Pd-Ni/Al₂O₃ catalysts determined from the results of H_T-O_T titrations (full lines) and on TPR of the oxidized surface (dashed lines).

from the variations in the effect of the metal particle size (16).

In the present method we also assume a lack of the oxygen-induced surface segregation of nickel (heat of oxygen adsorption on Ni—448 kJ/mole and on Pd—281 kJ/mole) (17). A considerable contribution of such an effect would confine the proposed method to the determination of the surface composition of Pd-Ni/Al₂O₃ catalysts in oxygen.

Summing up, the reactivity of the palladium surface oxidized at room temperature toward hydrogen and a lack of reactivity of the oxidized surface of nickel may be the basis for the method of determining the surface composition of Pd-Ni/Al₂O₃ catalysts. Using H_T-O_T titration reactions the share of the palladium surface atoms can be determined and by the TPR the share of the nickel surface atoms may be evaluated.

Good agreement of the results obtained by means of both chemisorption methods confirms their usefulness and applicability.

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Received April 21, 1983; revised February 3, 1984