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Some Electric Properties of Nickel-Chromia Catalyst Studied by the Contact Potential Method

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The dependence of the work function of the Ni-Cr_2O_3 system upon the concentration of the components and its change in different gaseous atmospheres is studied. The results are correlated with the catalytic activity of the nickel-chromia system for the isotopic exchange reaction between hydrogen and water.

INTRODUCTION

In recent years the nickel-chromia catalyst has been examined in detail (*1*, *2*), both because it is an active catalyst for the deuterium exchange reaction between hydrogen and water vapor (*3*) and for the more general interest that the transition metals promoted by oxides represent in heterogeneous catalysis (*4*).

Nickel-chromia samples, prepared by means of a known method (*3*) appear as a polycrystalline powder the grains of which (0.2–0.3 mm in diameter) consist of distinguished agglomerates of nickel and chromia in close contact. These agglomerates contain nickel microcrystals of average dimensions of the order of 10^2 Å and chromia microcrystals of average dimensions of the order of 10 Å.

The electrical conductivity measurements (*5*) have shown a metallic behavior for samples with high nickel content (100–96% Ni) and an abrupt transition to semiconductor behavior due to the semiconductivity of the chromia for samples with a nickel content less that 96%. The polyphasic aspect of this catalyst and the fact that its catalytic activity for the above-mentioned reaction has the highest value just in the range of the abrupt change of the electrical conductivity suggest that the contacts between its components would have an electronic role in its activity.

The present paper aims to complete the correlation between the electronic and the catalytic properties of the nickel-chromia system. For this reason, it is of great interest to know the dependence of the work function of the system upon the component concentrations and its change in different gaseous atmospheres.

EXPERIMENTAL

Because of the heterogeneity of the sample surfaces one may attribute to the nickel-chromia system only an average work function which has been determined by the contact potential method using a vibrating condenser apparatus described in a previous paper (*6*).

The layout of the vibrating condenser in the experimental tube of the apparatus is given in Fig. 1. The fixed plate of the electrostatically driven condenser is formed by the sample to be measured, and the mobile reference electrode is a gold-coated mica plate. The contact potential difference between these two plates, which value is equal to the difference of their work functions, is measured at the output of a selective amplifier system by a null method. The pastilled samples are 14 mm in diameter and about 1 mm in thickness. It is possible to measure a set of five samples under the same conditions of vacuum or controlled gaseous atmospheres between 20° and 200°C. There have been measured the variation of the contact potential difference between the catalyst and reference electrode as a function of its components concentration

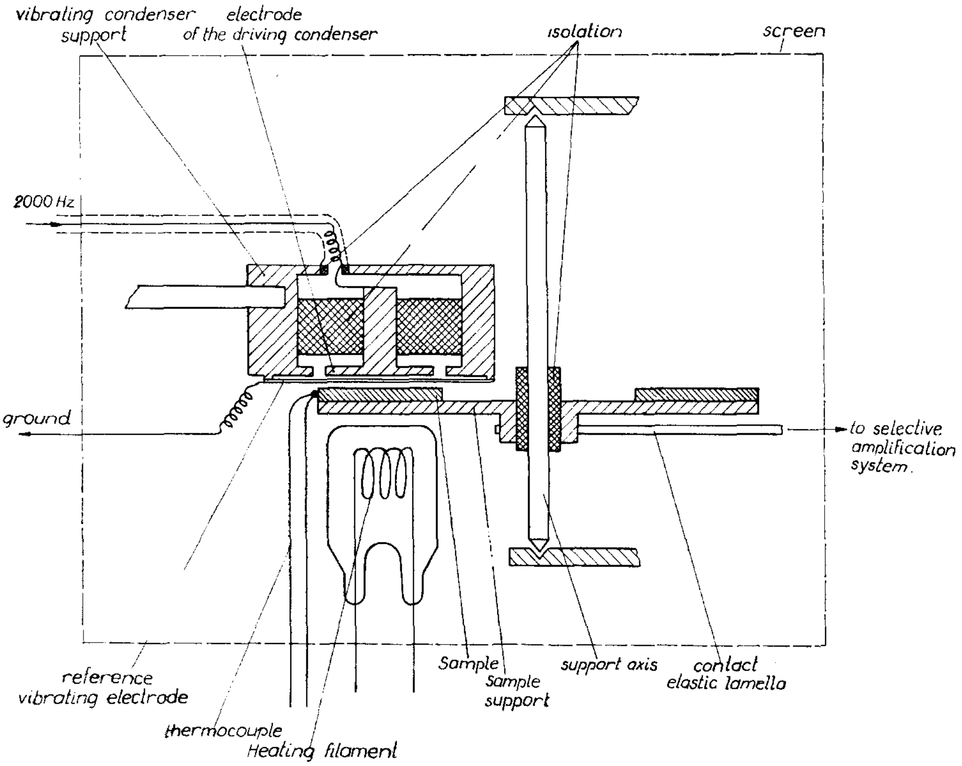

FIG. 1. Setup of the vibrating condenser.

and the changes of the contact potential difference in hydrogen and oxygen atmospheres. The measurements were performed in the following order:

(1) In order to reduce the superficial nickel oxide, the pastilled samples were maintained in purified flowing hydrogen at 150°C until the measured contact potential difference reached a constant value.

(2) The samples were then evacuated at the same temperature till a pressure of 10^{-4} torr was attained and then the contact difference potential was measured.

(3) At last, the measurements in flowing oxygen were carried out.

RESULTS

In Fig. 2 the measured contact potential differences between gold and nickel-chromia as a function of nickel concentration in vacuum (a), flowing hydrogen (b), and flowing oxygen (c) at room temperature are plotted. The average error in measurements was not higher than ± 10 mV. The sign of the measured contact potential difference indicates the electrical charging of the sample compared to that of the reference electrode. The sample has a negative or a positive charge when its work function (Λ_{sample}) has a higher or a lower value than that of gold (Λ_{gold}). Independent of the gaseous atmosphere, there has been observed a sudden increase of the contact potential difference (i.e., a sudden decrease of the work function) from the value corresponding to 100% Ni concentration to a maximum corresponding to about 93% Ni concentration, followed then by a slow decrease to the value of the contact potential difference between gold and chromia.

DISCUSSION

1. The Dependence of the Work Function of the Nickel-Chromia System on the Components Concentration

The dependence of the work function of the nickel-chromia system on the com-

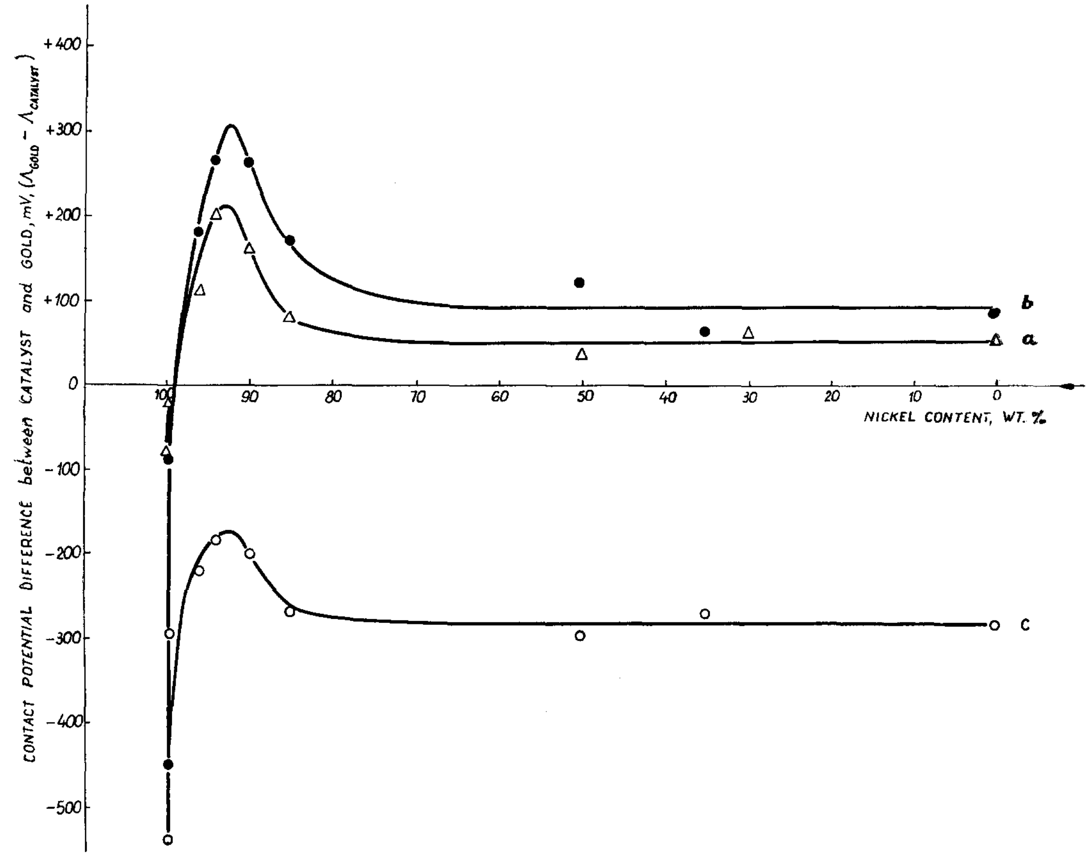

FIG. 2. Contact potential difference between the nickel chromia catalyst and gold vs. nickel concentration: (a) in vacuum; (b) in flowing hydrogen; (c) in flowing oxygen.

ponent concentrations may be observed from curve a, Fig. 2, obtained in vacuum. The shape of the curve may be explained if we admit that chromia in the samples with high nickel content is deposited on the surface of the nickel particles like a thin film of molecules polarized by the high electron affinity of the nickel phase. The sudden decrease of the work function is due to the fast increase of the surface coverage of the nickel particles by chromia. As the oxide concentration increases, the chromia begins to appear also like a bulk phase, screening more and more the nickel surface. After reaching a minimum, the work function of the system begins to be dictated by the oxide phase though the nickel concentration of the system is still high.

The model presented is in good agreement with the electrical conductivity measurements and the X-ray analysis, as has been related in previous papers (*5*, *7*). It has been shown that ranging from 100% Ni to 94% Ni, the size of the nickel crystallites decreases from about 600 Å to about 90 Å, a fine dispersion of the nickel occurring, determined by the structural promoter property of the chromia (Fig. 3). At the same time, in the range of 96–93% Ni, the electrical conductivity changes its character from metallic to semiconductor (Fig. 4, curve ●). These results are in agreement with the above assumption that the chromia is preferably deposited as a thin film on the surface of the nickel particles for high nickel concentrations and as a bulk phase for nickel concentrations lower than about 94%.

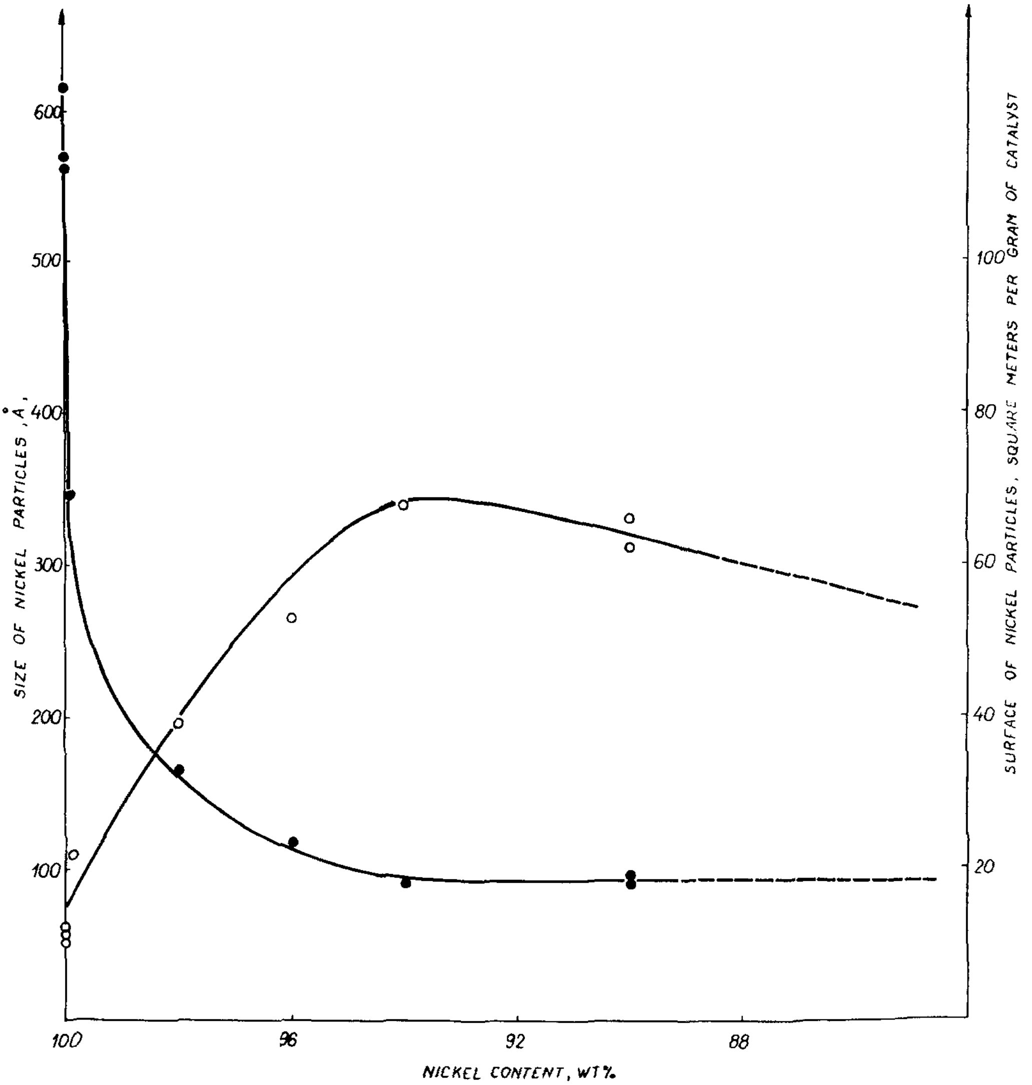

FIG. 3. Size of the nickel particles (●) and nickel surface area (○) vs. nickel concentration.

2. The Influence of Gas Adsorption on the Work Function

Owing to the physical and chemical heterogeneity of the sample surfaces we can admit that under the conditions mentioned the gas chemisorption is present in all its three forms ("weak," "strong acceptor," and "strong donor" form), one or the other of them prevailing. It is interesting to see how the character of the gas adsorption is influenced by the change of the surface structure.

As a result of hydrogen adsorption on pure nickel at normal pressure, the sample surface has got a considerable negative charge compared to that found in vacuum (Fig. 2, curve b). We can assert that hydrogen chemisorption on pure nickel takes place predominately in the "strong acceptor" form. The chromia deposited on the nickel grain surface as a dipole layer with outwardly positive charge begins to hinder the acceptor chemisorption of hydrogen, favoring donor character. A small amount of 0.2% chromia modifies to a great extent (300–400 mV) the negative charging of

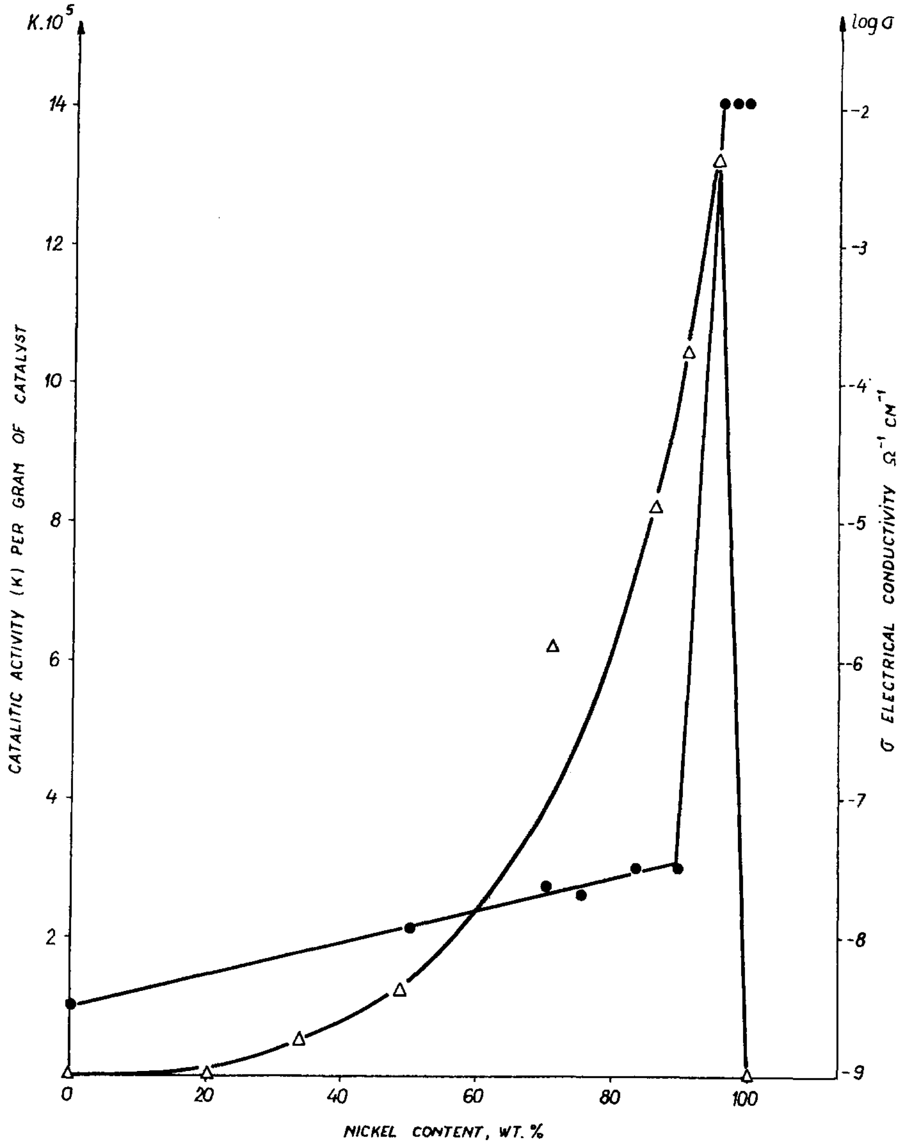

FIG. 4. Electrical conductivity (●) and catalytic activity in moles of deuterium per sec per g sample (△) of the nickel chromia catalyst vs. nickel concentration.

the sample in comparison with the charging of pure nickel. For samples with nickel concentration lower than 99%, the hydrogen chemisorption gets a donor character, charging the sample surface positively. As the bulk phase of chromia appears in the system, the hydrogen meets the contact boundaries between Ni and Cr_2O_3 phases on the sample surface. The equilibrium of these phases in contact has been established due to the equalization of their electrochemical potentials (ρ_{Ni} and $\rho_{Cr_2O_3}$) by a charge transfer from one phase to the other. As a result of this charge flowing, the metallic phase, having a work function (Λ_{Ni}) higher than that of the oxide ($\Lambda_{Cr_2O_3}$), gets an excess of electrons and the chromia (in our case being a p semiconductor) gets an excess of holes. The external electrical potentials (ψ_{Ni} and $\psi_{Cr_2O_3}$) of the phases in contact

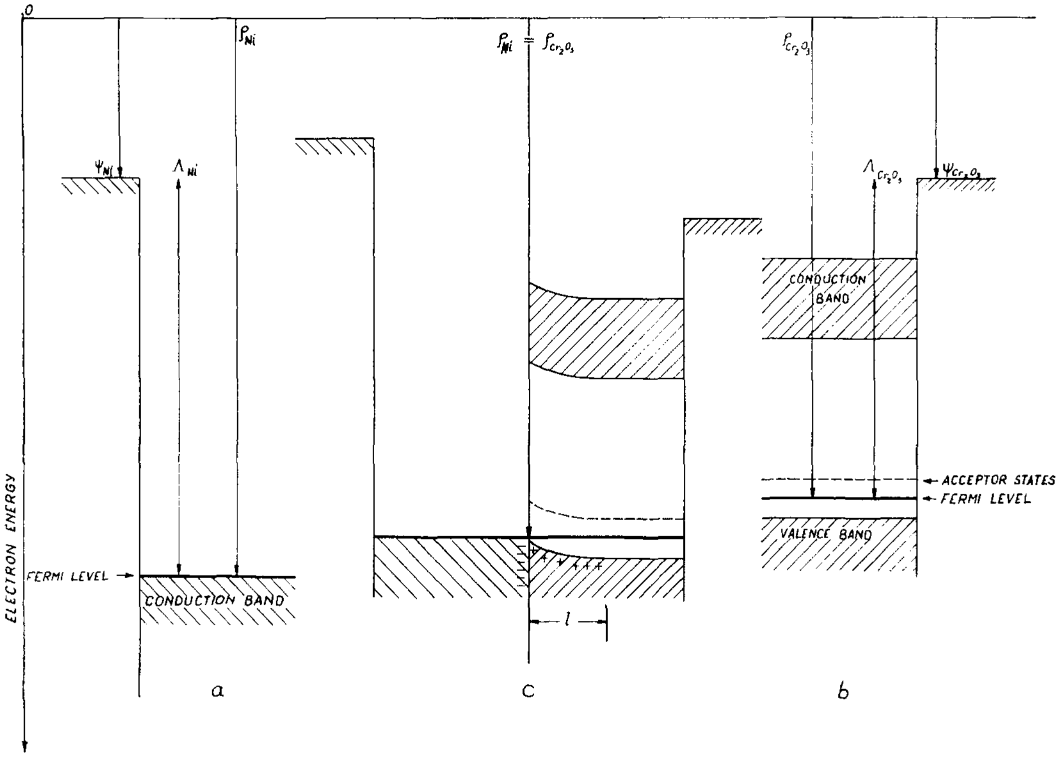

FIG. 5. Energy level diagram of metal p-type semiconductor contact with $\Lambda_{\text{metal}} > \Lambda_{\text{semiconductor}}$: (a, b) before contact is made, (c) after contact is made.

have also changed adequately (Fig. 5). At the contact surface of the chromia, a positive spatial charge extended in the bulk of the chromia phase has been formed at a distance equal to the screening length (l).

The presence of these positively charged domains favors the donor chemisorption of hydrogen the more so as the number of such regions increases. It seems to realize the highest number of contact points between the metallic and semiconductor phase for samples with a concentration of 92–93% nickel. For this concentration the positive charging of the surface is maximum (curve b, Fig. 2). The slow decrease of the degree of positive charging is determined by the presence of lower and lower superficial density of the contact points as the oxide concentration increases. For high chromia concentrations the curve b approaches the curve a; that means that at room temperature the adsorption of hydrogen on chromia has no essential effect on its work function.

In oxygen atmosphere, the surface of the samples becomes very negatively charged for the whole concentration range, the oxygen acting as an electron acceptor gas. In this case we could also observe that the coverage of the nickel grains by chromia occurs to a large extent even for samples with high nickel concentration.

The change in the work function of the system in hydrogen and oxygen atmospheres at the temperature of 130°C (the temperature at which the catalytic activity of this system was studied) has also been measured. No essential modification has been observed either in the value or in the position of the maximum of the measured contact potential difference.

The above results can be correlated with the catalytic activity of the nickel-chromia system. The catalytic activity per gram of catalyst has a very sharp maximum for the concentration of 94% nickel, as is shown in Fig. 4 (curve △). The work function measurements show that the increase of the activity may be attributed not only to a structural factor, i.e., the increase of the nickel surface area, when chromia is added, as was observed by X-ray analysis (Fig. 3), but also to an electronic factor. Thus, at the concentration for which the activity has the highest value, the nickel-chromia system has indeed the lowest work function and the hydrogen chemisorption makes it even lower. It is as if the deuterium exchange reaction between hydrogen and water vapor would be an electron acceptor type reaction and it would be facilitated by the presence of a system which can more easily donate the electrons. Taking into account this conclusion, it is expected that the oxygen (which increases the work function of the catalyst) behave itself as a poison for the mentioned reaction, as has already been observed experimentally (*8*).

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