ACTIVITY AND PHYSICAL PROPERTIES OF Ni/SiO$_2$ HYDROGENATION CATALYSTS

Horst KINZA[a], Ivo PASEKA[b] and N. M. POPOVA[c]

[a] *Central Institute of Physical Chemistry,*
Academy of Sciences of the GDR, Berlin, GDR,
[b] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 160 00 Prague, Czechoslovakia and
[c] *Institute of Organic Catalysis and Electrochemistry,*
*Academy of of Sciences of the Kazakh SSR, Alma-Ata, USSR*

The influence of the reduction temperature of Ni/SiO$_2$ catalyst on the amount of adsorbed hydrogen and on the hydrogenation rate of *o*-nitrophenol and sunflower oil has been followed. The total amount and two forms of adsorbed hydrogen have been determined by TPD and electrochemical cyclic galvanostatic charging methods. The properties of catalysts were further studied by the measurement of polarization curves of electrochemical oxidation and evolution of hydrogen. The correlation between the hydrogenation rates of *o*-nitrophenol and weakly adsorbed hydrogen on the one hand and that of sunflower oil and total amount of adsorbed hydrogen on the other hand has been found.

The already early revealed analogy between the behaviour of heavy metals as reversible hydrogen electrodes and as hydrogenation catalysts, and the importance of amount, binding strength and reactivity of adsorbed hydrogen with regard to the catalytic properties of technical hydrogenation catalysts[1−4] suggests the idea, to characterise these parameters not only by kinetic and adsorption methods, but by electrochemical methods too.

Nevertheless, there are many papers on the investigation of adsorbed hydrogen on catalysts by electrochemical methods (for a survey, especially for H on Ni, see *e.g.*[5]) on the one hand and by adsorption methods on the other hand, but almost no work to compare the results of both classes of methods on the same catalyst. The reason of this may be the peculiarities of technical hydrogenation catalysts: high dispersity of the active metallic phase distributed on a carrier, frequently an electrical insulator, require in every case a careful test, to what extent and by which electrochemical methods unequivocal results are quaranted with these catalysts. With respect to the Ni/SiO$_2$ hydrogenation catalyst Kt 6 500 (Leuna-Werke "Walter Ulbricht", GDR, precursor "Grünkorn", Kt 6 600) it was possible, by means of extremely slow (to awoid overvoltages on the catalyst) galvanostatic charging curves to determine the amount and the kinds of adsorbed hydrogen[5] and to compare the results with those from TPD (ref.[6]) and microcalorimetric measurements[7].

The aim of the present wotk was to investigate the relations between the amount, form and reactivity of absorbed hydrogen and the catalytic activity of the industrial catalyst Kt 6 500 in hydrogenation of *o*-nitrophenol (ONP) and sunflower oil. In order

to reduce the number of factors that may affect the mentioned properties, we examined a series of Ni/SiO$_2$ catalyst samples prepared from the same precursor Kt 6 600 by reduction in a hydrogen stream at 483 K $\leq T_{red} \leq$ 710 K for 4 or 8 h. The catalyst Kt 6 500 according to the conditions of the reduction and the stabilization degree contains 60 – 70% of nickel as Ni^0 and Ni^{2+}. The physicochemical properties of this catalyst are described in detail in refs[8-11]. The hydrogen adsorption was studied by the temperature-programmed desorption method (TPD) and by the cyclic galvano-static charging (GCC). The electrocatalytical activity was determined by measuring the specific exchange current of the reaction

$$H_2 + OH^- \; \rightleftharpoons \; 2\,H_2O + 2\,e \quad (H.E.R.) \qquad (A)$$
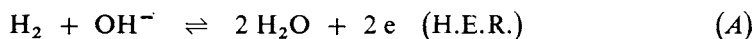
The catalysts were tested in sunflower oil pressure hydrogenation and in potential--controlled o-nitrophenol hydrogenation at normal pressure. All properties of catalysts were followed as functions of the reduction temperature. The temperature programmed desorption (TPD) was investigated over a temperature range from 213 to 623 K on samples obtained by the reduction of the precursor *in situ.*

EXPERIMENTAL

All the electrochemical measurements were carried out at room temperature; the hydrogenation of o-nitrophenol (ONP) at 30°C. For the measurement of specific exchange currents, the reduced catalyst in aqueous suspension was brought to a potential + 150 mV (RHE) by careful oxidation with air pulses, so that after drying it was no longer pyrophoric. Preliminary experiments showed that after this treatment the catalyst could be reduced electrochemically again without changing its initial specific metallic surface and the amounts of both forms of adsorbed hydrogen deter-mined by GCC. For measurements, a few milligrams of the catalyst mixed with graphite and PTFE were pressed onto a round nickel grid of 10 mm in diameter. So prepared solid discs were used in the form of the rotating electrode to measure the polarization curves. From the measured polarization curves in the range of potential $\pm$ 10 mV, the polarization resistances were determined and hence the specific exchange currents per 1 g of catalyst were evaluated.

The charging curves were measured on freshly reduced samples which before measurement had been additionally saturated with hydrogen in the measuring cell at $\pm$ 10 mV (RHE) for 20 h.

In the galvanostatic determination (GCC) of adsorbed hydrogen the application of current densities below 10 mA g^{-1} of catalyst ensured that these are far lower than the exchange current densities of the hydrogen reaction which are about $2-3 \cdot 10^{-6}$ A cm^{-2} or 8 A g$_{Ni}^{-1}$ (ref.[5]). Graphical differentiation of the obtained charging curves yields the adsorption curve of hydrogen as a function of potential, since the primarily obtained charge may be used to calculate, using the Faraday constant, the adsorbed hydrogen amount. In this way, we obtained similarly as in the TPD method the distribution of the adsorbed hydrogen according to its binding energy.

The sunflower-oil hydrogenation was carried out in a stirred autoclave at 403 K, with an initial pressure of 3 MPa. The hydrogenation occurred in the kinetic region as it was proved experi-mentally from the linear dependence of the k_{oil} on the weight of catalyst

$$dp(H_2)/dt = k_{oil}c_{oil}^0\, p(H_2)\,. \qquad (1)$$

From the variation in pressure with time the rate constant k_{oil} was calculated to be first order with respect to hydrogen. The potential-controlled hydrogenation of ONP was run in a microreactor equipped with a platinum vibrating stirrer on which the same potential was established as on the catalyst particles and with an automatic titration device (Radiometer) for dosing the reactant[12]. o-Nitrophenol was hydrogenated in 1M-KOH at potentials between $+5$ and $+60$ mV (RHE).

RESULTS AND DISCUSSION

A typical hydrogenation rate of o-nitrophenol (ONP) as a function of potential is shown in Fig. 1. The experimental curves can be linearized by a semiempirical method[7] and their average slopes were used to calculate rate constants $\bar{k}$ for all catalyst samples.

The temperature programmed desorption curves showed (Fig. 2) that hydrogen is chemisorbed in two formes, H_I and H_{II}, in addition to the apparently physically adsorbed form H_0 which is desorbed at $T_{des} \lesssim 273$ K. The presence of two adsorbed forms of hydrogen is also manifest in pseudocapacity curves calculated from galvanostatic charging curves (Fig. 3). Both method indicate that the major portion of hydrogen is adsorbed in the strongly bound form H_{II}.
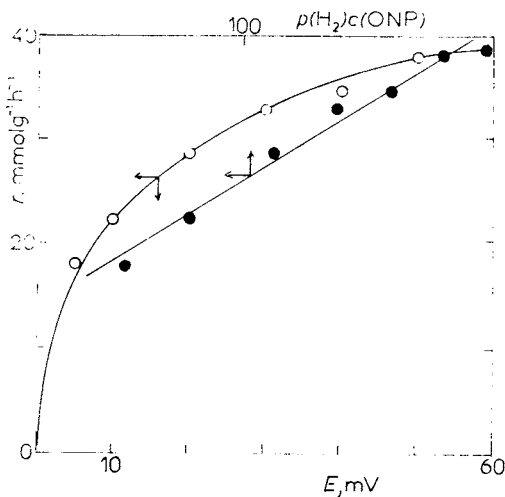

FIG. 1

The rate of the o-nitrophenol hydrogenation as a function of controlled potential. ○ Experimental values, ● linearized values
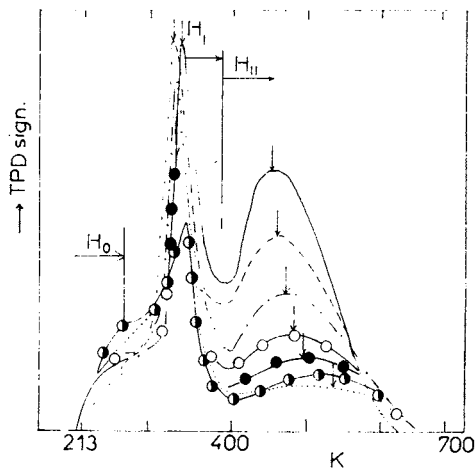
FIG. 2

TPD curves of catalysts reduced at various T_{red}, — 513 K, ----- 533 K, —·—·— 553 K, –○–○– 593 K, –●–●– 653 K, –◑–◑– 693 K, ········ 723 K

The maximum quantities of the total chemisorbed hydrogen determined by both methods are almost the same, *i.e.* 10 to 20 cm^3/g of unreduced catalyst.

Totally different patterns of total adsorbed hydrogen in dependence on T_{red} are, however, observed for the amounts of adsorbed hydrogen as determined by the two methods, particularly for the strongly bound form H_{II}. While in TPD method the increase in T_{red} gives rise to strong, monotonous decrease in the amount of H_{ad} (Fig. 4), the quantity of adsorbed hydrogen determined by GCC shows, after very small initial values, a steep increase on catalysts reduced at $T_{red} \gtrsim 553$ K, and maximum at 623 K (Fig. 6). The same steep increase is observed for the exchange current i_0 (Fig. 8) but no such behaviour is found for the catalyst activity in either of the hydrogenation reactions. The parallelism in the electrochemical determinations indicates that observed properties arise from the common cause which is inherent both in a very nature of Ni/SiO₂ catalyst precursor which is not reduced uniformly. The reduction of the basic carbonates begins already at the temperature lower than 550 K, whereas the nickel hydrosilicates only begin to be reduced at essentially higher temperatures[13]. This can also be seen from Fig. 5 providing a comparison between gravimetric reduction curves for the catalyst and a well defined nickel silicate. One must also consider that in the temperature range $T_{red} \leqq 553$ K the original
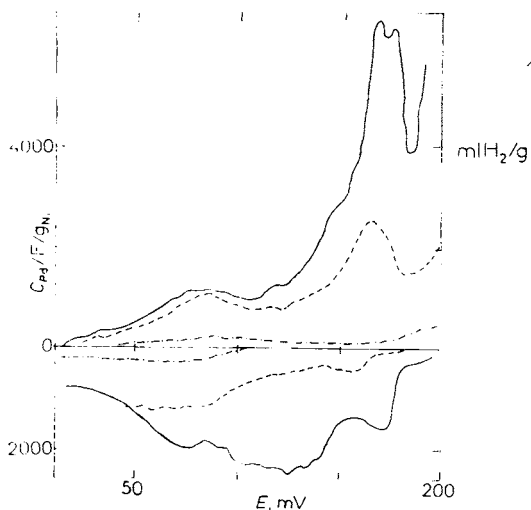

FIG. 3

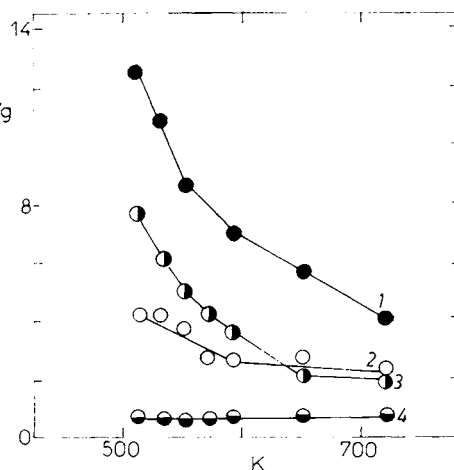Differential pseudocapacities C_{pd} evaluated from the galvanostatic charge measurements

FIG. 4

The amounts of various forms of H_{ad} (in ml H_2 per gram of catalyst) in dependence on T_{red} as determined by TPD method. 1 $\sum H_{ad}$, 2 H_I, 3 H_{II}, 4 H_{phys}

carbonate layer is in the form of metallic particles supported on SiO_2 and still unreduced and hence insulating nickel silicate carrier. This highly dispersed form of nickel is accesible to thermal desorption and catalytic measurements but can hardly be detected by the electrochemical methods owing to the wide separation of the metallic particles. Only as the silicate-bound nickel compound is reduced starting at 533 K, gradually contributing to the electronic conductivity of the catalyst, an increasing proportion of the metallic nickel surface can be detected by electrochemical methods. In this period, however, the highly disperse nickel particles, arisen from the non-silicate nickel compounds, already begin to sinter. At temperatures above 660 K the influence of the sintering will be greater then the still proceeding reduction. This hypothesis is supported by results of a further series of experiments in which samples reduced twice as long were examined over the same temperature range by GCC measuring (Fig. 6, dashed lines). The measured values are almost twice those found after 4 h reduction, especially at the lower T_{red}. Moreover, a somewhat higher maximum was reached on catalysts which were reduced at lower T_{red} since the longer reduction time not only increases the degree of reduction but also enhances the effect of sintering at a given temperature. For these reasons, the correlation between the electrochemically determined
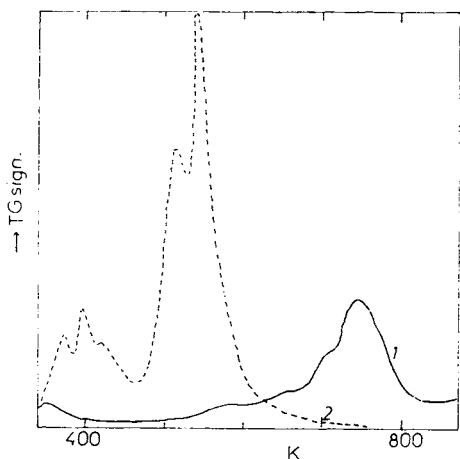

FIG. 5

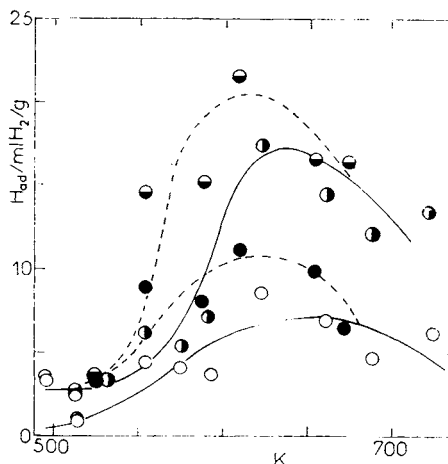Thermogravimetric curves of reduction (Kt 6 600 2), (Ni antigorit 1)

FIG. 6

The amounts of adsorbed hydrogen (in ml H_2 per gram of catalyst) determined by GCC method after 4 or 8 h reduction as function of T_{red}; cathodic values. ——— 4 h, - - - - - 8 h, ○, ● H_I ◑, ◔ $\sum H_{ad}$

and catalytic properties is meaningful only for those samples which have been reduced at $T_{red} \geq 553$ K. This restriction does not, of course, hold for TPD method. This opinion is further supported by direct determination of the reduction degrees of the catalyst 6 600 reduced at various temperatures[14].

Fig. 7 shows a plot of the amounts of the total $\sum H_{ad}$ as determined by TPD method, the weakly bound H_{ad} as calculated from the cathodic section of GCC, and the constants of the sunflower-oil and o-nitrophenol hydrogenations as a function of the reduction temperatures. Since the o-nitrophenol hydrogenation was carried out in the potential range $5 < E < 60$ mV (RHE), only the H_{ad} amounts determined in this range have been included in the figure. The plot of the specific exchange current of the hydrogen evolution-oxidation reaction in the dependence of T_{red} together with the hydrogenation constants is shown in Fig. 8.

A close correlation is to be noted between the constants of the sunflower-oil hydrogenation and the total amounts of H_{ad} as determined by thermal desorption. The weakly bound portion of adsorbed hydrogen, on the other hand, shows no correlation with the hydrogenation rate constant. The o-nitrophenol hydrogenation rate constants which remain within experimental scatter almost unchanged over
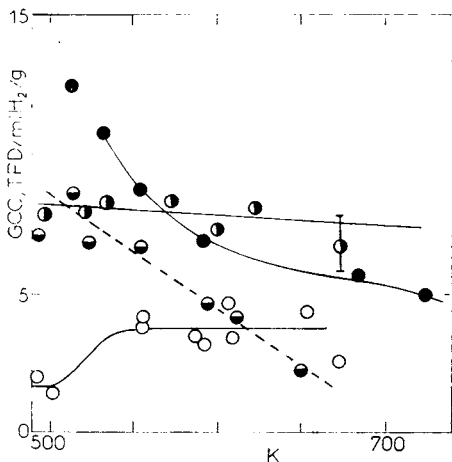

Fig. 7

Comparison of various properties of catalysts. ● Total adsorbed hydrogen determined by TPD, ○ adsorbed hydrogen H$_I$ by GCC; catalytic activity for ◐ sunflower oil hydrogenation, ◑ ONP hydrogenation
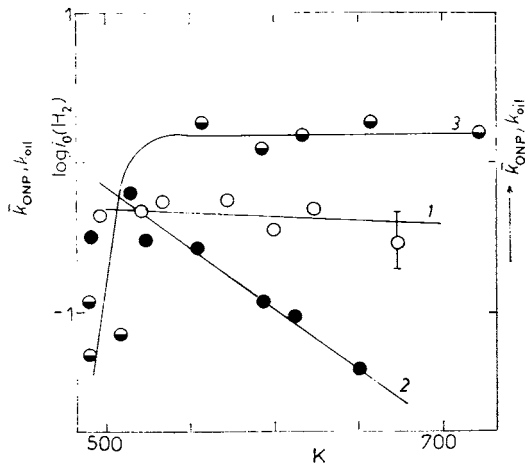
Fig. 8

Comparison of the specific exchange current $i_0(H_2)$(A g^{-1}) of the hydrogen redox reaction with hydrogenation rate constants. 1 $\overline{k}_{ONP}$, 2 k_{oil}, 3 $i_0(H_2)$

the whole T_{red} range cannot be correlated with either the strongly bound nor total $\sum H_{ad}$ amount, whether determined by TPD desorption or GCC. Relatively the best correlation is found between the hydrogenation of ONP on one hand and the specific exchange current and weakly bound H_{ad} as determined by GCC on the other hand which likewise show no significant variation at $T_{red} > 553$ K.

The fact that the two hydrogenation reactions are so differently correlated with hydrogen adsorption is undoubtedly connected with their quite different reaction mechanism. Unlike the hydrogenation of oils, where the hydrogenation process, *i.e.* the attachement of H_{ad} to the —C=C— bond, occurs in a purely catalytic way, the nitro compound hydrogenation in an alkaline medium proceeds, according to the view of many authors[15,16] by direct electrochemical reduction involving transfer of electrons to the adsorbed aci-form of the nitro compound. This means that the hydrogenation process represents an electrochemical, short-circuited cell in which hydrogen is adsorbed and oxidized on the catalyst surface:

$$H_2 \;\rightleftharpoons\; 2\,H_{ad} \qquad\qquad (B)$$

$$2\,H_{ad} \;\rightleftharpoons\; 2\,H^+ + 2\,e \qquad\qquad (C)$$

The electrons generated in reaction (C) are taken by the adsorbed nitro compound which is thus reduced. Owing to the experimental arrangement of the process when only such amount of ONP is fed into the reaction vessel that is able be immediately hydrogenated at a given potential without its significant change, the stationary concentration of ONP is so low that the reduction process proceeds in the diffusion range. It means that the surface concentration of ONP is almost zero and rate of this cathodic reduction step is independent of the potential. So, the rate controlling step of the whole hydrogenation reaction is the rate of the anodic part of the reaction, *i.e.* the rate of the anodic oxidation of hydrogen. For these reasons also the overall hydrogenation rate is determined by the dependence of the hydrogen oxidation rate on the potential. As the rate of this hydrogen oxidation reaction depends mainly on the exchange current of this reaction it is reasonable to expect the significant correlation between i_0 and the rate of catalytic hydrogenation of ONP. The work of Angely and coworkers[17] has indicated that the rate of hydrogen oxidation depends on the number of active centres of nickel to which only weakly bound form of adsorbed hydrogen is attached; it is therefore reasonable to expect also correlation between H_I and the activity of ONP hydrogenation.

The close correlation between the rate of hydrogenation of oil and total amount of $\sum H_{ad}$ (Fig. 7) can be understood taking into account that the total amount of adsorbed hydrogen as determined by TPD method is proportional to the metallic nickel surface. As the hydrogenation rate is zero order in respect to the oil conc-

centration it means that the surface of a catalyst is almost completely covered by adsorbed fatty acid molecules. Hence, the observed correlation exists between reaction rate constant and the amount of chemisorbed oil molecules. As, on the other hand, the reaction rate is first order in respect to hydrogen pressure, one can assume, according to a slight modificated opinion of (ref.[18]), that the limiting step of oil hydrogenation on this type of Ni/SiO₂ catalysts is the reaction between chemisorbed oil molecules and weakly adsorbed hydrogen.

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