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Investigation of Properties of the Metallic Nickel Surface in Mixed Ni-MgO Catalysts

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In this work we report the results of an investigation of the properties of a series of Ni-MgO catalysts with total nickel content in the range from 2.6 to 87.8 wt %; the catalyst was prepared by thermal decomposition of corresponding mixed oxalates *in vacuo*. The properties of metallic nickel in the catalysts were studied by means of hydrogen chemisorption at different temperatures (beginning with 78°K) and the values obtained are compared with the catalytic activity of these catalysts for benzene hydrogenation.

METHODS

The dehydration and the subsequent decomposition of mixed oxalates was carried out in a vacuum apparatus. The dehydration of mixed oxalates was performed at 180–200°C, at which temperature the dehydration is completed in 2–3 hr and the decomposition of dehydrated oxalates has not yet occurred. The temperature at which the mixed oxalates start to decompose at a measurable rate depends on the composition of the mixed oxalates and varies for the different compositions between about 400°C for the pure magnesium oxalate and 240°C for nickel oxalate. The decomposition of the dehydrated samples of mixed oxalates was carried out so that while the temperature of the sample was increased the pressure of the gaseous products of decomposition was practically constant and did not exceed 1×10^{-2} mm Hg. The end of decomposition was indicated by a rapid decrease in pressure in the apparatus; all samples were subsequently heated *in vacuo* for 5 hr at 460°C. During this period the pressure in the apparatus dropped to a value always lower than 10^{-6} mm Hg.

The determination of metallic nickel was made by the analysis of CO and CO_2 formed during decomposition of the particular mixed oxalate *in vacuo*. CO_2 was frozen in a trap cooled by liquid nitrogen (−195°C) and CO in a following trap containing active charcoal and also cooled by liquid nitrogen. A very good separation of the two gases was obtained in this way. During the decomposition the system of traps was used for obtaining vacuum, the pumping speed being comparable to the pumping speed of a good mercury diffusion pump. After the finish of decomposition the vessel with the sample was sealed off, and the trapped gases were separately evaporated into a calibrated volume, the amounts of CO and CO_2 being calculated from the measured pressure in this volume at a given temperature. If these amounts are expressed in moles (denoted as m_{CO} and m_{CO_2}), the formula $(m_{CO_2} - m_{CO})/2$ then gives directly the amount of metallic nickel (moles) in a given weight of the sample.

The determination of chemisorbed hydrogen at 78°K was made in an adsorption volumetric apparatus provided with mercury cutoffs and a freezing trap for mercury vapors in the vicinity of catalyst sample. The samples for chemisorption measurements were sealed off in evacuated vessels with breaker seals which were broken after the evacuation of the apparatus immediately before hydrogen adsorption measurements. Hydrogen adsorption at

78°K was measured at a constant pressure of 4 mm Hg for all samples and always 30 min after hydrogen admission. The adsorption proceeded rapidly—70 to 80% of this (30 min) amount was taken up during the first 10 min, which shows that the rate of adsorption is comparable to that on evaporated films. However, this is merely to illustrate the rapidity of adsorption; only 30 min values were used in Table 1, Fig. 1, and the Discussion. A more detailed description of the apparatus together with further results of the study of chemisorption on powder Ni catalysts will be communicated in a following paper.

The catalytic activity of the catalysts was determined for the hydrogenation of benzene in a flow, all glass, vacuum apparatus in a way described in our previous work (*1*). The hydrogenation of benzene was carried out at 40°C at atmospheric pressure and with the molar ratio of $H_2:C_6H_6$ equal to 9:1.

RESULTS

The results obtained in the manner described are presented in Table 1. The contents of total and metallic nickel are given in weight per cent. Catalytic activities of metallic nickel in Ni-MgO catalysts are expressed as moles of benzene reacted at 40°C in 1 min on 1 g of metallic nickel. The amount of hydrogen adsorbed at 78°K (30 min) is expressed in moles of hydrogen adsorbed on 1 g of metallic nickel. No measurable adsorption of hydrogen was found on MgO prepared by Mg-oxalate decomposition under the same conditions. In the last column of Table 1 are given ratios of catalytic activity and the amount of chemisorbed hydrogen related to 1 g of metallic nickel.

TABLE 1

Number of catalyst	Content of Ni_{total} (wt %)	Content of Ni_{metal} (wt %)	Catalytic activity $r_{Ni_{metal}} \times 10^4$ $\left[\frac{\text{mole } (C_6H_6)}{\text{min} \times \text{g}(Ni_{metal})}\right]$	Amount adsorbed $m_{H_2} \times 10^4$ $\left[\frac{\text{mole } (H_2)}{\text{g}(Ni_{metal})}\right]$	$r_{Ni_{metal}}/m_{H_2}$ $\left[\frac{\text{mole } (C_6H_6)}{\text{mole } (H_2) \times \text{min}}\right]$
1	2.6	0.42	5.0	—	—
2	5.3	1.05	4.7	34	0.14
3	11.7	5.03	4.5	12	0.38
4	19.9	10.1	4.1	—	—
5	29.7	19.5	2.6	8.9	0.29
6	33.4	22.6	2.2	8.0	0.28
7	42.9	32.3	1.5	5.5	0.27
8	53.9	45.5	1.0	3.6	0.28
9	63.6	55.9	0.73	2.9	0.25
10	77.3	72.8	0.49	1.6	0.31
11	87.8	86.5	0.30	1.1	0.27

DISCUSSION

The constant ratio $r_{Ni_{metal}}/m_{H_2}$ proves that the rapid hydrogen chemisorption at 78°K is directly proportional to the catalytic activity for benzene hydrogenation under given conditions and for the given series of catalysts in the whole range of compositions studied, and that a certain connection exists between the amount of rapidly sorbed hydrogen at 78°K and catalytic activity.

It follows from the values shown in Table 1 that both quantities, i.e. the amount of chemisorbed hydrogen and the catalytic activity of 1 g of metallic nickel, increase gradually with decreasing metallic nickel content in the catalyst; this finding is in agreement with a gradual increase of the surface of 1 g of metallic nickel with its decreasing content in the catalysts, in other words with increasing dispersity of the metallic nickel. Similar results were obtained in the work (*2*) where the grain size of metallic nickel in the catalysts under consideration was determined from X-rays and thermomagnetic measurements. In the work cited, a calculation was made of the surface area of metallic nickel, based on the estimated grain size, on the assumption of cubic particles. From surface area obtained in this way a calculation of specific sorption of hydrogen was made and the value of 5×10^{-2}–7×10^{-2} cm^3/cm^2 was obtained. If this value is compared with the corresponding value measured on evaporated nickel films (21×10^{-2}–22×10^{-2} cm^3/m^2) (*3, 4, 5*), it appears that the unit area of metallic nickel in Ni-MgO catalysts adsorbs one-quarter to one-third of the amount adsorbed by unit area of evaporated nickel film; this would, according to Roberts and Sykes (*6*), correspond to about 30% purity of the surface of metallic nickel.

For comparison of the extent of hydrogen chemisorption in the investigated series of catalysts with hydrogen chemisorption on evaporated nickel films, the isobars of hydrogen adsorption were measured on some of the catalysts at 4 mm Hg, beginning with the temperature of 78°K, in the ordinary way. In order to make the comparison of isobars, the amount of chemisorbed hydrogen was related to 1 m^2 of the surface area of metallic nickel, determined by the mentioned method (*2*) for the Ni-MgO catalysts. Figure 1 shows, for illustration, the isobar of specific hydrogen chemisorption on catalyst No. 9 and that on evaporated nickel film taken from ref. (*5*). The shape of the isobars is analogous for nickel in the Ni-MgO catalyst and for evaporated nickel. The good agreement of the upper branch of the isobars shows that no considerable amount of reducible impurities (namely oxygen) is present in the surface of our catalyst, since these impurities increase the magnitude of activated hydrogen adsorption and thus shift the upper branch of the isobar towards higher magnitudes of hydrogen adsorption (*5, 7*). This finding

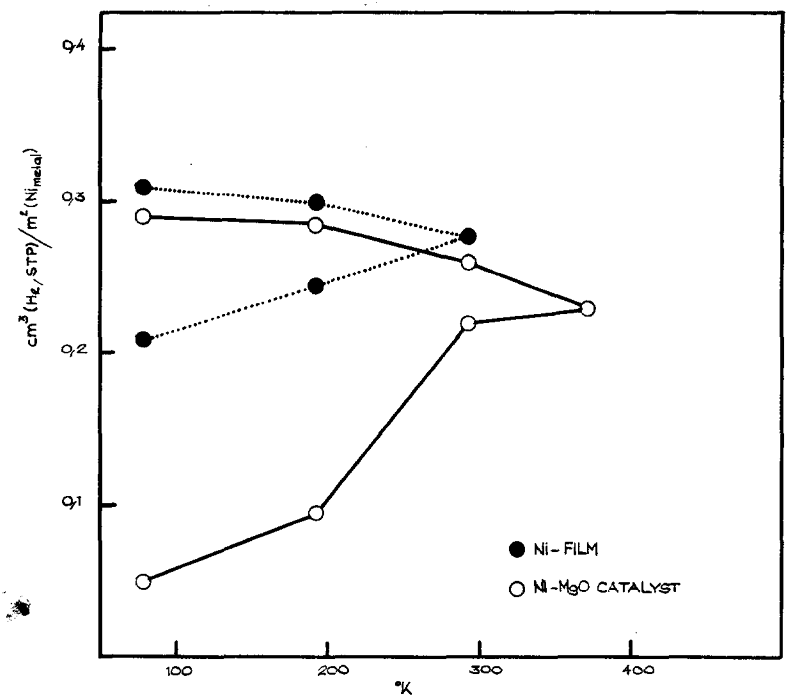

FIG. 1. Comparison of measured isobars of chemisorption of hydrogen on Ni-MgO catalyst No. 9 and on evaporated Ni film (*5*). In the lower branches of isobars are plotted amounts adsorbed on a fresh sample at subsequently increased temperatures, beginning with 78°K; in the upper branches, amounts adsorbed when decreasing the temperature from 20°C (film) and/or 100°C (powder) are plotted. The pressure was maintained at 4 mm Hg.

supports the idea that the bonded nickel which is contained in the catalysts is strongly bonded in the lattice of magnesium oxide (*1*) in the form of mixed oxide and is not therefore capable of reduction under decomposition conditions. The existence of this oxide is confirmed by, among other methods, the X-ray analysis.

The considerable adsorption of hydrogen at 78°K indicates that there is a relatively large surface area on the catalyst, upon which the hydrogen adsorbs with a very low activation energy. It follows from our measurements that this part of the surface participates substantially in the catalytic activity for the hydrogenation of benzene. Such a rather high chemisorption of hydrogen at low temperature has been so far reported in the literature only for such nickel catalysts whose surface has been subjected to an intensive reduction by hydrogen at 500°C (*6, 7*). In our case the adsorption power may bear a connection with the influence of the reducing gaseous medium (CO) which is created during the decomposition of Ni-Mg oxalates. The presence of CO during decomposition probably restricts the formation of bonded oxygen in metallic nickel and, at the same time, its low partial pressure does not give an opportunity for the creation of nickel carbide, or carbon, to a greater extent. Another factor favoring the creation of a relatively clean surface is the heating of the catalysts to a temperature of 460°C *in vacuo* since at this temperature the existence of Ni_3C is thermodynamically excluded (*8*) and, as Dell (*9*) and Zettlemoyer (*10*) have shown, regeneration of the metal surface may occur.

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