

The Promoting Action of Chromia for Nickel Catalysts

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The promoting action of the addition of varying amounts of chromia to nickel catalysts has been investigated, using the deuterium exchange reaction between hydrogen and water vapor as a test reaction. A correlation between activity and nickel surface area was performed. This latter was measured by means of hydrogen chemisorption at room temperature. The values of the BET surface area from the krypton adsorption isotherm at -196°C were also determined. Then, measurement of electrical conductivity in flowing hydrogen was carried out.

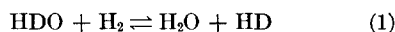
The observed structural promoting effect exhibits a very rapid increase at lower chromia content. In the same range, the activity per unit surface area of nickel increases by more than two orders of magnitude, the samples having a metallic behavior. At higher chromia content, both the nickel dispersion and the specific activity are unaffected by higher concentrations of the chromia promoter, the samples having a semiconductor behavior.

INTRODUCTION

In heterogeneous catalysis several examples of increase of the activity of metallic catalysts by means of promoters are known. The promoter can induce an increase both of the metallic surface area and the activity per unit surface area of the finely dispersed metal (1). Nevertheless, for the characterization of the promoter action, few available data on the simultaneous measurements of the activity and metallic surface area are given in the literature. As for the supported metals (2) there is an additional difficulty in determining the surface area of the metal itself. This must be distinguished from the total surface area, as determined by the BET method.

Recently, we have been interested in the behavior of nickel catalysts which contain small amounts of chromia. In this paper we present the experimental results (over a wide range of chromia contents) for the activity of the promoted nickel in the exchange reaction of deuterium between hydrogen and water vapor in connection with the metallic surface area measure-

ments. For this exchange reaction, the nickel catalyst is active (3), and the chromia induces a large increase of its catalytic activity (4). But no attempt to correlate the activity and the nickel surface area was made. The test reaction used in the present paper has the following advantage: The reaction products differ only isotopically from the initial reagents. Thus, during the reaction, no important changes in the nature of the catalyst-reagents system appear along the catalyst bed. The reaction rate measurements have been performed within the range of small isotopic content so that the D_2 and D_2O concentrations are very low (5). Thus, it may be considered that only the reaction (1) takes place.



The nickel surface area is usually determined by the selective chemisorption of hydrogen (2, 6), oxygen (7), or carbon monoxide (8). We have not used the chemisorption of carbon monoxide because it may be chemisorbed in two forms, the bridge form occupying two sites and the

linear form occupying only one site (9). We have used the hydrogen chemisorption in a similar manner to that described previously by Taylor, Yates, and Sinfelt (10). We have also measured the metallic surface area from the oxygen chemisorption, according to the method of Lyubarskii and co-workers (7). The oxygen uptake is about twice as large as the hydrogen uptake for all catalysts studied. But, the oxygen uptake is larger when larger oxygen portions are introduced into the sample cell. This fact can be attributed to the oxidation in the bulk due to the high adsorption heat of the oxygen on the nickel (11). Therefore we present here only data on hydrogen chemisorption.

We have also determined the electrical conductivity of various nickel-chromia catalysts and their BET surface area. Krypton rather than nitrogen was used because at 77°K nitrogen chemisorption occurs on chromia (12).

EXPERIMENTAL

1. Catalyst Preparation

The studied catalysts of various chromia contents were prepared by coprecipitation with sodium carbonate from a mixture of aqueous solutions of chromium and nickel nitrate. The precipitate was filtered, washed with bidistilled water, dried at 105°C, ground, sorted, and calcined in flowing nitrogen at 320°C.

After cooling at room temperature, the nitrogen stream was removed and hydrogen was passed through the oxide mixture at a flow rate of 1000 cm³/min. The temperature was then slowly increased (up to 350°C in 8 hr) in order to prevent superheating during the reduction process (13). The catalyst was maintained in flowing hydrogen for 5 hr at 350°C; then it was cooled in the same atmosphere and passivated at room temperature in flowing nitrogen with low oxygen concentration.

After stabilization, the catalysts were again sorted. For all measurements powdered catalysts of 0.2–0.3 mm size were employed.

During the filtration and washing of the

precipitate, losses of nickel as well as of chromium may occur. These losses in filtered solutions were determined by usual chemical methods. It was observed that both the nickel and chromium solubility from the precipitate was very low, so that the chromium-to-nickel ratio in the catalyst was practically the same as the initial ratio from the mixture of chromium and nickel nitrate.

The temperature and time necessary for complete calcination and reduction processes were established by thermogravimetric measurements.

Nickel nitrate, chromium nitrate, and sodium carbonate obtained from E. Merck, A. G. Darmstadt, were used. The electrolytic hydrogen employed was purified in a Deoxo unit containing palladium catalyst in order to remove trace amounts of oxygen. The formed water was then removed by a trap which was cooled in Dry Ice.

2. Kinetic Measurements

a. Apparatus and materials. The reaction rate measurements were carried out in a flow system at atmospheric pressure. The reactor (Fig. 1) was a vertical glass tube having two connected parts: the saturator and the catalytic cell. A fritted glass disk (0.4 cm in diameter) was used to support 0.1 g catalyst in the reactor. It was thermostated by means of a benzene vapor jacket; the saturator was thermostated to the boiling point of methanol. The isotopic concentration of the water from the saturator was 5.35 at. % deuterium, thus practically only reaction (1) occurs. A 100 cc/min hydrogen flow was bubbled through the water from the saturator in order to obtain its saturation. The hydrogen–water vapor mixture was passed through the catalyst bed. After reaction, the hydrogen stream was dried in a silica gel trap, and its deuterium content was analyzed by a chromatographic unit (14). As checked by a previous test, the silica gel trap does not affect the deuterium concentration of the gas sample by a possible exchange between the HD formed in the reaction and the water or the surface hydroxyl groups present on the silica. The chromatographic col-

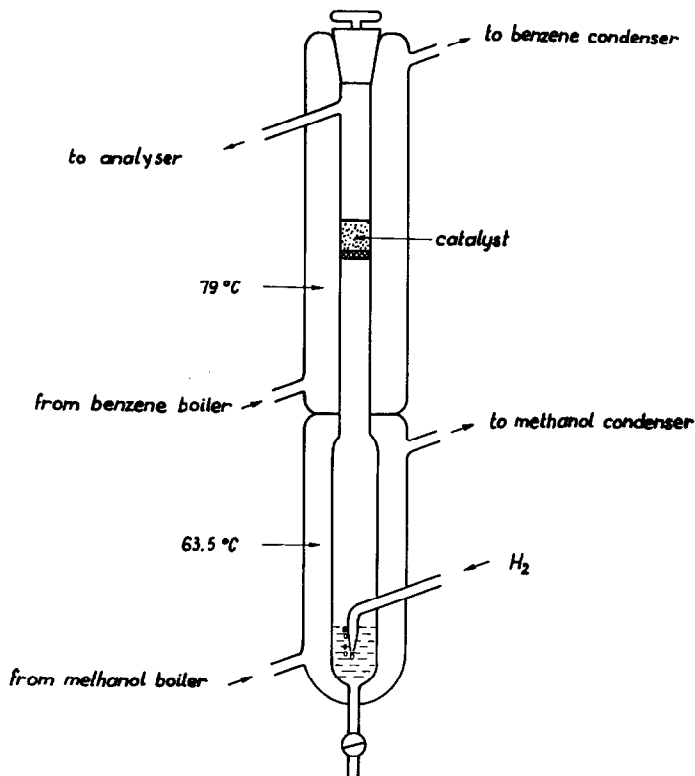


FIG. 1. Dynamic exchange reactor.

umn was 1 m in length and 0.7 cm in diameter. The column was packed with charcoal and was operated at 25°C. A thermal conductivity detector was used. As carrier gas in the chromatographic unit hydrogen (20 cc/min) was employed.

Electrolytic hydrogen (about 0.005 at. % deuterium) was introduced both in the reactor tube and in the chromatographic unit. It was previously purified in a Deoxo unit and dried in a silica gel trap.

b. Estimation of the catalytic activity.

The catalytic activity of each sample was determined after the measurements of its nickel surface area. As described in Section 4, the measurement was preceded by a testing of the completeness of the reduction process. After finishing the nickel surface area measurement the catalyst sample was again passivated and transferred into the reactor tube. The sample was then reactivated in flowing hydrogen at 150°C for 2 hr, without heating the saturator. The reactivation temperature is not essential, in so

far the activity is concerned. As shown in previous experiments it affects only the time of reactivation.

The reaction rate r (moles of deuterium transferred per gram of catalyst during a second) for reaction (1) was determined from the relation*

$$r = \frac{F}{[\alpha + (1/\beta)]W} \ln \frac{n_e - n_0}{n_c - n} \quad (2)$$

where F represents the flow rate of the hydrogen through the reactor, in mole/sec; W

* This equation can be obtained by integration of the kinetic equations $F dn/dw = -r(\alpha n - N)$ and $\beta F dN/dw = r(\alpha n - N)$. [See, for instance, K. Cohen, in "The Theory of Isotope Separation as Applied to the Large-Scale Production of U²³⁵" (G. M. Murphy, ed.), p. 133, McGraw-Hill Book Co., Inc., New York, 1951], where N represents the deuterium concentration in the water vapor while all the other notations have already been explained in the body of this paper. The integration is facilitated (16) by using the isotope conservation $n + \beta N = \text{const}$ and the equilibrium concentration n_e [Eq. (3)].

represents the weight in grams of the catalyst charge; α is the value of the equilibrium constant for the exchange reaction (1); β is the ratio of partial pressures of the reagents $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$; n_0 and n are the values of deuterium concentration of the hydrogen before and after reaction, respectively; and n_e is the deuterium concentration in hydrogen at equilibrium, after the reaction has been performed. The value of the equilibrium concentration n_e results from

$$n_e = \frac{[N_0 + (1/\beta)n_0]}{[\alpha + (1/\beta)]} \quad (3)$$

where N_0 is the value of the deuterium concentration of the water from the saturator. At 79°C, the value of α is 2.77; at 63.5°C the value of β is 0.315.

The relation (2) is valid for the reaction (1) because it is of the first order (15) in the range of small deuterium concentrations. The validity of the relation (2) was previously verified experimentally (16). It was also demonstrated that under the experimental conditions described above, the outer diffusion processes are very rapid as compared to the reaction on the nickel surface. But, at lower temperatures, the vapor sedimentation in pores because of capillary condensation can appear. It affects the reaction rate which is measured in the whole catalyst bed (16). At higher temperatures, the speed of the inner diffusion processes becomes comparable with the rate of the exchange reaction on the active surface. Previously (17), we have described the experimental conditions under which neither the effects of the capillary condensation nor those of the inner diffusion appear. Thus, we chose the following values for the saturation and reaction temperatures 63.5°C (the boiling point of methanol) and 79°C (the boiling point of benzene), respectively.

3. Total Surface Area Measurement

For all the catalysts studied the adsorption isotherm of krypton verified the BET equation if the extrapolated value at 77°K for the equilibrium vapor pressure of the

supercooled liquid krypton was introduced in this equation.

The value of the total surface area was also calculated using the Kaganer calculation method (18) for small degree of coverage:

$$\log V = \log V_m - \gamma[RT \log (p/p_e)]^2 \quad (4)$$

where V is the volume (STP) adsorbed at pressure p ; V_m is the adsorbed volume (STP) corresponding to a monolayer, p_e is the equilibrium vapor pressure; and γ is the adsorption coefficient. The values obtained for V_m according to this equation agreed with the BET values.

For the cross-sectional area of the adsorbate molecule, a value $\sigma_{\text{Kr}} = 19.5 \text{ \AA}^2$ was used, as described previously by Mainwaring and Stock (19).

The high-purity krypton used for the BET determination was obtained from Farbwerke Hoechst, A.G., Frankfurt (M).

4. The Metallic Surface Area Measurement

Each sample of previously passivated catalyst, weighing about 2 g, was put in a vacuum apparatus. The sample cell had two valves in order to permit the flow of the hydrogen through the sample.

The sample was again reduced overnight at 350°C in flowing hydrogen (200 cc/min), evacuated at the same temperature till a pressure of 1.10^{-5} torr was attained (6) and then an adsorption isotherm at room temperature was carried out. All these operations were repeated for the same sample till a constant and reproducible value of the surface area was obtained. This procedure was performed for each catalyst sample. In this way, it was possible to test the completeness of the reduction process.

In the measurement of the hydrogen adsorption isotherms, the procedure adopted was to admit a known quantity of hydrogen to the adsorption cell. The rate of the pressure decrease is negligible after about 1 hr, indicating the attainment of equilibrium (20). In Fig. 2 the adsorption isotherm of nickel at 25°C is plotted;

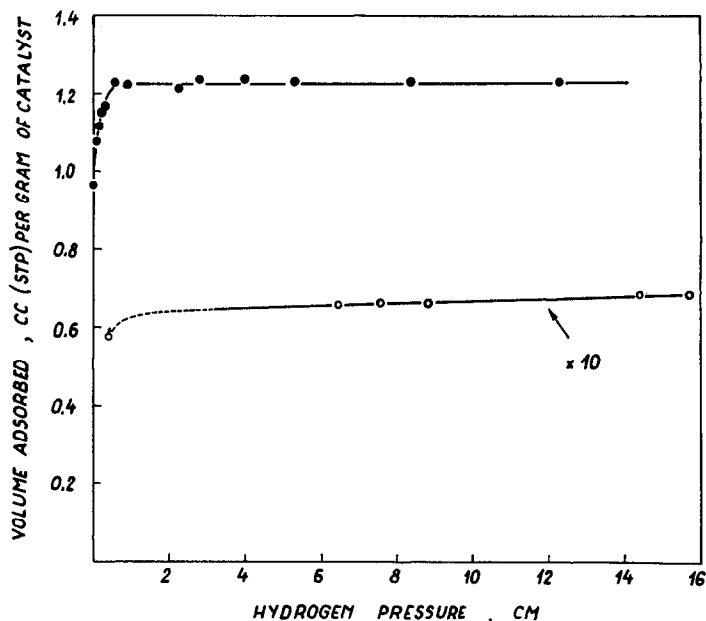


FIG. 2. Adsorption isotherms for H_2 on nickel at room temperature: ●, 100 at. % nickel, 0 at. % chromium; ○, 80 at. % nickel, 20 at. % chromium. For this last isotherm, the adsorbed amount must be read multiplying by a factor of 10.

it may be observed that experimental points of different successive determinations are placed along the same curve. On the same figure is represented also the adsorption isotherm for the 20 at. % chromium sample. It may be observed that saturation is approached at hydrogen pressures above 5 mm. At equilibrium pressure corresponding to the monolayer, the value of 10 cm is employed (20). From Fig. 2 it is possible to observe that above 5 mm the slope of the adsorption isotherm is negligible for nickel and remains small for nickel-chromia catalysts, so that the choice of 10 cm as the monolayer point seems reasonable.

Following Klemperer and Stone (21), we have based the evaluation of the nickel surface area on the assumption that hydrogen is dissociatively adsorbed on every available nickel site and the superficial nickel site population is 1.54×10^{19} atoms/ m^2 , which gives a value for the amount of adsorbed hydrogen of 0.286 cm^3 (STP)/ m^2 nickel.

For nickel, a comparison between the BET area and the metallic area using the

hydrogen chemisorption gives the following values: $4.3 \text{ m}^2/\text{g}$ through BET measurement and $4.4 \text{ m}^2/\text{g}$ through hydrogen chemisorption.

Electrolytic hydrogen was introduced into the apparatus both for the reduction and for the adsorption measurements. It was previously purified in a Deoxo unit and dried in a Dry Ice trap.

5. Electrical Conductivity Measurement

The electrical conductivity was measured by putting the powdered catalyst between two electrodes and applying a direct current (22). The voltage (4 V) was applied to the sample only during the measurements of conductivity in order to minimize the polarization effects. The measurements were made in a stream of hydrogen (100 cc/min) at atmospheric pressure. The catalyst was placed between perforated platinum electrodes; the upper one was weighted with a perforated stainless-steel cylinder.

Electrolytic hydrogen, purified in a Deoxo unit and dried in a silica gel trap, was used.

TABLE 1
ACTIVITY AND SURFACE AREA OF CATALYST FOR THE DEUTERIUM EXCHANGE
BETWEEN HYDROGEN AND WATER VAPOR

$\frac{\text{No. of Cr atoms}}{\text{Total No. of Ni + Cr atoms}} (\%)$	Activity in moles of deuterium per sec per g sample, $r \times 10^4$	Specific surface area of nickel, (m ² /g sample)	Percentage dispersion of nickel η	Total surface area, (m ² /g sample)	Specific activity in moles of deuterium per sec per m ² of nickel, $r_s \times 10^6$
0	0.0025	4.4	0.7	4.3	0.057
0.1	0.0175	6.2	0.9	7.9	0.28
0.2	0.045	5.4	0.8	8.9	0.83
1	0.30	11.1	1.7	18.3	2.70
2	0.69	18.1	2.8	32.4	3.82
3	1.05	23.0	3.6	62	4.56
5	1.20	20.6	3.3	59	5.83
10	0.89	22.9	3.9	103	3.89
15	1.93	27.0	5.0	120	7.15
20	1.67	23.4	4.7	150	7.15
30	1.20	16.5	3.9	230	7.28
40	1.27	18.0	5.0	282	7.06

RESULTS

The chromia content of the prepared catalysts is listed in the first column of Table 1. It is expressed as number of chromium atoms divided by the total number of nickel and chromium atoms.

In the second column of Table 1 there are listed the values of the reaction rate r , expressed in moles of deuterium exchanged between water vapor and hydrogen, per second and per gram of catalyst.

The values of nickel surface area (expressed as square meters of nickel per gram of catalyst) determined from hydrogen chemisorption at room temperature are given in the third column of Table 1.

In Table 1 are also reported the values of nickel dispersion η , defined as the ratio of nickel surface atoms to the total number of nickel atoms in the sample.

The values of the total surface area (expressed as square meters per gram of catalyst) determined from krypton adsorption at -196°C by means of the BET calculation method are tabulated in the fifth column of Table 1.

The values of specific activity r_s , defined as ratio of the reaction rate r to the nickel surface area are listed in the last column of Table 1. These values are expressed as moles of deuterium exchanged between water vapor and hydrogen per

second and per unit of nickel surface area.

In Fig. 3 are plotted the values of electrical conductivity of the samples, obtained in flowing hydrogen, at 80° , 180° , and 280°C , respectively.

DISCUSSION

As regards the activity, there is a large promoting effect. The highest values of activity are larger to about three orders of magnitude than the value provided by a pure nickel catalyst.

At first, the chromia shows a structural promoting effect; the available surface of nickel increases by almost one order of magnitude. By means of promoting, the exposure degree of nickel increases from 0.7% to about 5%.

But, the chromia presence in the catalyst gives rise also to another effect; the catalytic activity per unit of nickel surface area increases more than two orders of magnitude.

Both the structural effect and the increase of specific activity exhibit a saturation tendency. The essential increase of activity is attained within the range of few percent chromia. At higher chromia content, the dispersion degree of nickel and also the specific activity remain constant within experimental accuracy.

The total surface area of catalysts in-

creases gradually as a function of chromia content. No saturation tendency occurs, in contrast with the specific activity and with the nickel surface area. The chromia surface area (calculated as the difference between total and nickel surface area) is

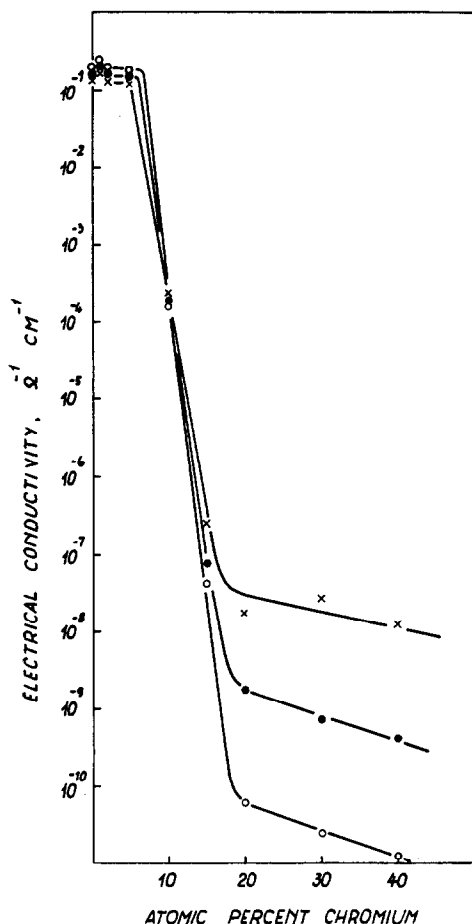


FIG. 3. Electrical conductivity of promoted nickel in flowing hydrogen, as a function of promoter concentration (chromia content is expressed as atomic percent chromium): ○, at 80°C; ●, at 180°C; ×, at 280°C.

plotted in Fig. 4 as a function of chromia content. A straight line is obtained. This shows, at least at higher chromia content, that the chromia dispersion does not depend on its content. From the slope of this line, an average value of 570 m^2/g of chromia may be calculated for the chromia surface area. At lower chromia

content, the most interesting region, this estimation method is too imprecise and it cannot report reliable values for the chromia dispersion. Therefore, a direct method, for instance, measurement of ultraviolet absorption of the Cr^{6+} obtained from chromia after its oxidation (23), seems to be preferable.

At lower chromia content, as far as the activity increases, the reduced samples have a metallic behavior; the values of electrical conductivity are large and slowly decreasing as the temperature increases. The samples with higher chromia concentration are semiconductors; the values of electrical conductivity are small and vary directly with the temperature. At 80°C, the electrical conductivity decreases more than ten orders of magnitude. The sudden change of electrical conductivity occurs in the region corresponding to the end of the increase for the specific activity.

Concerning the increase of nickel dispersion, an explanation can be made regarding the peculiarities of the reduction process. Before its reduction, the nickel is highly dispersed as nickel oxide. Thus, the calcined sample, which contains only nickel oxide, has a value of surface area of about 270 m^2/g (determined from the krypton adsorption isotherm), while the nickel surface area resulting after reduction of the sample was only 4.3 m^2/g . Therefore, the reduced nickel arisen in many nickel oxide crystallites contributes to the formation of a larger nickel crystallite, during the recrystallisation process. For the promoted catalysts, this agglomeration can be partially avoided, due to the few percent of finely dispersed chromia contained in the catalysts. Further increase of chromia content can induce only an increase of the total surface area, the nickel dispersion remaining unchanged. Chromia can not be included in the nickel bulk on account of its large size as compared to the interatomic distance of the nickel lattice (24).

Turning to the results on the specific activity for the promoted nickel, various explanations can be given as regards its increase.

At first, we can suppose that all the

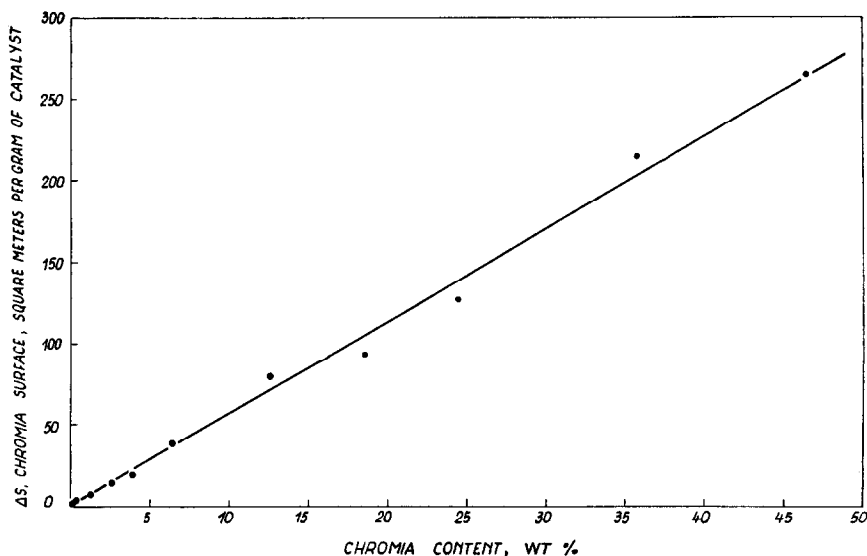


Fig. 4. Chromia surface area in promoted nickel catalysts (determined as difference between total surface area and nickel surface area) as a function of chromia content.

superficial nickel atoms are in fact active centers. By promoting, the surface of a nickel crystallite can keep chromia as a superficial impurity. New active centers (with larger turnover number) appear and the larger the chromia content is the more of these centers there are. Thus, after the saturation with chromia of the nickel surface, the activity per unit surface area of nickel becomes unaffected by the chromia content because the number of those active centers is proportional to the number of superficial nickel atoms.

On the other hand, we can expect that the contact points between nickel and chromia crystallites may come into play as new and very active centers (25), especially for the "demanding reactions," as Boudart and co-workers (26) have pointed out. The decrease in size of the nickel crystallites due to the structural promoting effect of chromia induces an increase of the number of such active centers. But, in this case, the number of nickel-chromia contact points is generally not proportional to the surface area of nickel.

Finally, the catalytic activity per unit surface area of the nickel can increase with decreasing size of the nickel crystallites. The investigations on the benzene hydro-

genation activity over Ni-SiO₂ catalysts, reported by Selwood, Adler, and Phillips (27) and those on the ethane hydrogenolysis over nickel on silica-alumina, reported by Carter, Cusumano, and Sinfelt (28), seem to confirm such a dependence for the supported catalysts whose surface area was varied by sintering. The results of the present investigation (at lower chromia content) indicate that the catalytic activity per unit surface area of nickel increases simultaneously with the increasing dispersion degree of nickel. Afterwards, irrespective of the chromia content, various samples have a well-defined value both of specific activity and nickel dispersion. These results seem to be in agreement with the idea of correlation between specific activity and crystallite size.

In order to decide on the right explanation, more information is required concerning the correlation between the specific activity and the active surface area for the promoted metals.

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