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Specific Catalytic Activity of Nickel in Hydrogenation of Carbon Dioxide to Methane

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This paper deals with the correlation between activity of nickel catalysts and their structure. The structure of nickel, chromium(III) oxide, and a model series of Ni/Cr_2O_3 catalysts was studied by low-temperature adsorption of nitrogen and oxygen chemisorption at 22°C. Oxygen uptake in the rapid stage of adsorption was found to be a proper measure of the number of nickel surface atoms in the samples. The chosen test reaction proceeds on all samples investigated according to the equation $r = kc_{CO_2}^{1/2}$. Chromium(III) oxide alone is inactive in the given reaction. The catalytic activity was expressed as a rate constant related to 1 g of the sample (k_g) as well as a rate constant related to 1 m^2 of nickel of the sample ($k_{S_{Ni}}$). While the k_g values varied in dependence on the composition about thirtyfold, the $k_{S_{Ni}}$ values varied less than twofold, so that it was possible to represent them for all the samples investigated by one Arrhenius straight line. The results obtained show that only nickel is the active component of the catalysts under study, whereas Cr_2O_3 is a structural promoter. In this paper an attempt is also made to characterize the present state of investigation of specific activity and its significance in catalysis.

1. Introduction

The relationship between the structure and activity of solids belongs to the most interesting problems of catalytic chemistry. For metals the important question is whether their activity in a given reaction depends on their forms, e.g., if they are in the form of an evaporated film, powder, or if they are supported. With multicomponent catalysts, where the metal is mostly combined with an oxide support or promoter, there exists the problem of whether the components form surface compounds together (e.g., of the type of spinels), or whether they act as separated substances on the surface. In such a case it is interesting to ascertain whether it is only the metal itself which is the active component of the catalyst, and what is the role of the oxide. To be able to answer all these and similar questions, it is necessary to investigate the so-called specific catalytic activity, i.e., the activity related to the unit of the total surface area of the catalyst, or, in the case of multicomponent catalysts, to the unit of the surface area of one of the the components (most frequently the metal). For studies on the specific catalytic activity a convenient method for the determination of the surface area of the separate components must be available. Therefore considerable attention now is given to the development of methods for the determination of the surface area of the separate catalyst components, especially for that of the metal component in such catalysts in which the metal is combined with an oxide support, or promoter (*1*).

The aim of the present paper is the endeavor to contribute to the solution of the problems connected with investigations on the specific catalytic activity. A model series of Ni/Cr_2O_3 catalysts and the reaction of selective hydrogenation of CO_2 to CH_4 was selected as the subject of these studies. The system mentioned is interesting from a

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practical viewpoint, too, as Ni/Cr_2O_3 catalysts are suitable for the removal of O_2, CO, and CO_2 from the N_2–H_2 mixture for the synthesis of ammonia (*2*); in this reaction it is the carbon dioxide which is hydrogenated more slowly than all other oxygen-containing impurities.

2. EXPERIMENTAL

Ni (Sample 1), Cr_2O_3 (Sample 8), and a series of Ni/Cr_2O_3 catalysts with subsequently lower Ni contents (Samples 2 to 7) were used for investigations on structure and activity. The composition of the samples is listed in Table 1 (Section 3, *C*). Samples 2–7 were prepared by coprecipitation of basic nickel carbonate and chromium(III) hydroxide from a mixed solution of nickel nitrate and chromium(III) nitrate by means of sodium carbonate. Samples 1 and 8 were prepared in a similar way from a solution of the relevant nitrate. Details on this preparation are described in a previous paper (*2*). The dried samples were calcined at 300–350°C for 2 hr and before activity or adsorption measurements they were reduced in a hydrogen flow at a final temperature of 300°C. The course of the reduction was followed by means of measurements of water content behind the catalyst. Some of the measurements were performed after reduction with hydrogen alone, in other experiments hydrogen was dosed into the flow of an inert gas (N_2). The reduction régime has no influence either on the structure or on the activity of the samples, if the reduction proceeds in such a way that the heat produced by the reduction can be dissipated. The total reduction time amounted to 10 to 15 hr.

Data on activity of the samples were obtained by measurements of the hydrogenation kinetics of carbon dioxide to methane in the presence of a large excess of hydrogen. The reaction was studied in a flow system and the data were obtained using a differential reactor with recirculation of the reaction mixture as well as an integral reactor. Reaction rates were measured in input CO_2 concentration range 5–25×10^{-5} moles/liter on 0.6 to 0.8 mm grains within a temperature interval of 150–220°C. Preliminary measurements have demonstrated that under the above conditions the reaction proceeds within the kinetic region. A scheme of the apparatus and details on the measurements of reaction kinetics are described in a previous paper (*3*).

Data on the structure of the samples were obtained by measurements of the total surface area by means of nitrogen at -196°C and of the amount of oxygen uptake at 22°C. The adsorption measurements were performed in a static vacuum apparatus described previously (*4*). The samples were freed from the gas at 300°C up to a final vacuum of the order of 10^{-6} torr before the surface area measurements. The surface area of the samples was calculated on the basis of the BET isotherm using the value of $\sigma_{N_2} = 16.2$ Å^2. The fact that nitrogen can be used for measurements of the total surface area of nickel catalysts was established previously (*4*). Before the determination of oxygen adsorption, nitrogen was removed from the surface by evacuation (the final pressure in the apparatus was again of the order of 10^{-6} torr). Oxygen adsorption was established from pressure changes at constant volume and final oxygen pressure of 50–100 torr.

3. RESULTS

A. Kinetics Measurements

At a high excess of hydrogen the hydrogenation of CO_2 on Samples 1 to 7 proceeds as a unidirectional selective reaction to methane and the reaction rate depends only on the CO_2 concentration. Sample 8 (Cr_2O_3) did not show any measureable activity at a temperature of 240°C either. In Fig. 1 some data showing the dependence of the reaction rate on the CO_2 concentration are presented which were obtained by measurements in the differential reactor with recirculation. It follows from Fig. 1, that on Samples 1, 4, and 5 the reaction is a one-half order with respect to CO_2. Therefore data obtained by means of the integral reactor were evaluated using an integrated form of the rate equation for a unidirectional one-half order reaction:

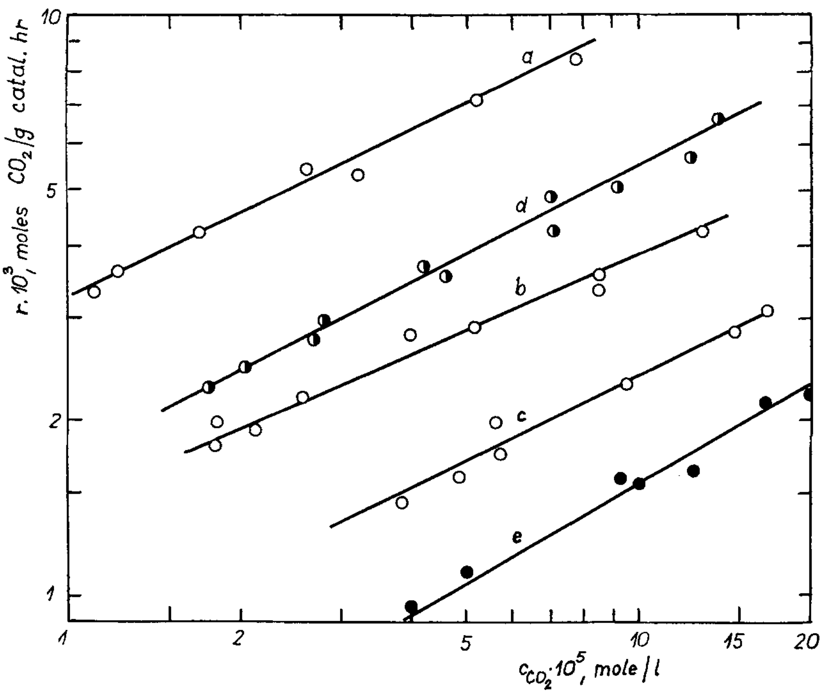

FIG. 1. Reaction rate of CO_2 hydrogenation as a function of CO_2 concentration: a, Sample 5 at 200°C; b, Sample 5 at 175°C; c, Sample 5 at 160°C; d, Sample 4 at 175°C; e, Sample 1 at 200°C.

$$k = \frac{2F}{W}\left(N_{CO_2}{}^0\,\frac{RT}{P}\right)^{1/2}\left[1 - (1 - \eta)^{1/2}\right] \quad (1)$$

where F represents the feed rate of reaction mixture in moles/hr; W, the weight of the catalyst in grams; $N_{CO_2}{}^0$, the initial mole fraction; and η the fraction of CO_2 converted to CH_4, $\eta = (N_{CO_2}{}^0 \text{-} N_{CO_2})/N_{CO_2}{}^0$. As the values of rate constants determined for various CO_2 concentrations did not change with the concentration monotonously, it can be stated that the CO_2 hydrogenation proceeds under the given conditions on all samples of nickel catalysts according to the kinetic equation

$$r = kc_{CO_2}{}^{1/2} \quad (2)$$

The average values of the rate constants found for various samples within a temperature range of 150–220°C are listed in Table 2 in Section 3, *D*).

B. Adsorption Measurements

The determination of the number of nickel surface atoms on the basis of oxygen adsorption at 22°C proved applicable in our previous studies of oxygen adsorption on nickel powder (*5*). Our previous results as well as further measurements some of which are presented in Fig. 2 for illustration lead to the following conclusions about the nature of oxygen adsorption.

a. Adsorption of oxygen on nickel and Ni/Cr_2O_3 catalysts. The adsorption of oxygen on nickel is appreciably exothermic and therefore a direct introduction of oxygen to the sample does not lead to any significant deviations from the isothermal nature of the process only in those cases in which the total adsorbed amount is small. Experiments performed in another connection (*6*), e.g., demonstrated, that the extent of oxygen adsorption on nickel is practically independent of the introduction rate within an interval of 0.5 to 60 min. To ascertain the isothermal nature of the adsorption, on the samples showing a large oxygen adsorption a controlled introduction of this gas was performed (dotted part of the curves in Fig. 2). The established oxygen uptake on nickel at 22°C corresponding to two layers

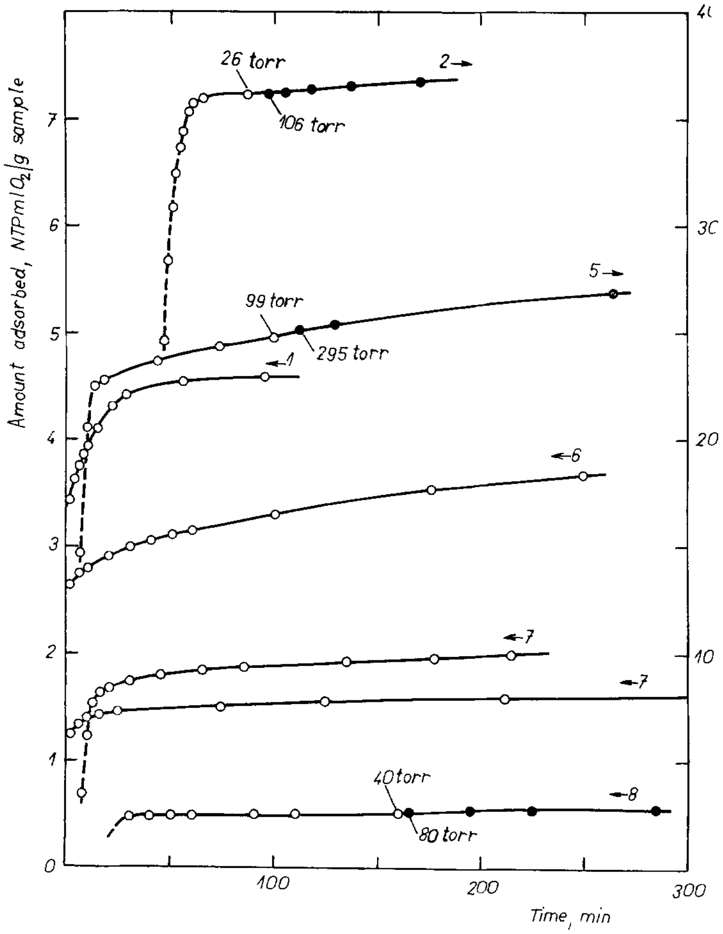

Fig. 2. Oxygen adsorption kinetics at 22°C.

of adsorbed oxygen atoms is in good agreement with data of other authors (*7–12*). It follows from Fig. 2 that from a kinetic point of view adsorption proceeds in two stages. In the rapid stage with an adsorption rate unmeasurable under the given experimental conditions, most of the adsorbate is adsorbed almost instantly. In the slow stage, corresponding to an increasing oxygen incorportion, a stationary state is attained. however, no adsorption equilibrium can be established, which is demonstrated by the values determined after longer time intervals. Stationary amounts of adsorption were used for nickel surface area calculations. Figure 2 also illustrates the fact that oxygen adsorption (more precisely its incorporation) does not depend on oxygen pressure within the range investigated. Average adsorption data obtained by measurements on a larger number of samples of the same type are shown in Fig. 3 in Section 3, *C*.

b. Adsorption of oxygen on chromium(III) oxide. In multicomponent catalysts similar to our samples adsorption on the oxide component in metal surface area determinations is negligible in most instances (*1*). To investigate this problem in some detail, oxygen adsorption was studied on chromium(III) oxide, too. The unreduced sample did not show (after the evacuation at 300°C to a pressure of 10^{-6} torr) any measurable oxygen adsorption. After the reduction with hydrogen at 300°C this sample changed color from the original black to green and

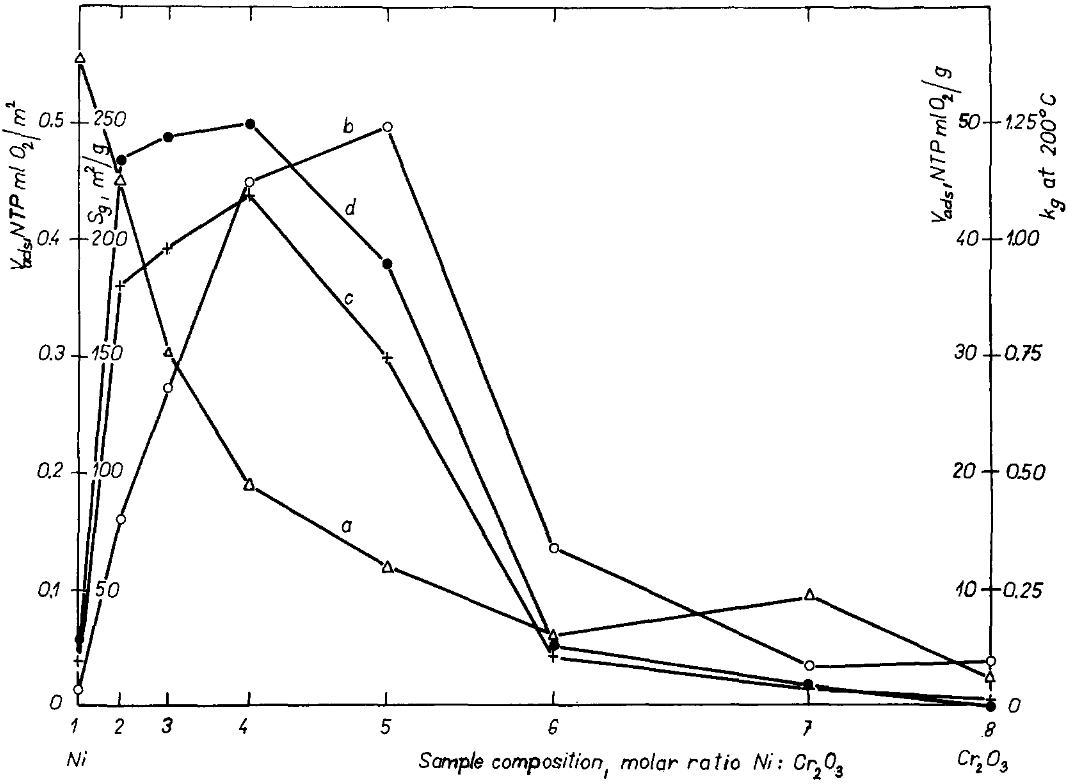

FIG. 3. Data on structure and activity of samples: △ (a), oxygen adsorption in ml O_2 NTP/m² sample; ○ (b), specific surface area in m²/ g sample; + (c), oxygen adsorption in ml O_2 NTP/g sample; ● (d), activity as k_g at 200°C in moles $CO_2^{1/2}$ liter$^{1/2}$/g sample hr.

at 22°C it adsorbed, on the average, 0.024 ml O_2 NTP/m² Cr_2O_3. No quantitative data were found in the literature for the adsorption of oxygen on Cr_2O_3 at 22°C. A comparison with the data on the amount of excess oxygen in differently treated Cr_2O_3 samples (*13*) can to a certain degree testify to the reality of the measured values.

Treatment	Excess oxygen	
	Moles/g (*13*)	After recalculation to ml O_2 NTP/m²
Oxygen at 500°C	141	0.09
Oxygen at 350°C	104	0.066
Air at 110°C	3	0.00192

As our samples were treated in the air at 300°C it can be assumed that the adsorption of O_2 on the reduced samples represents a process of their reoxidation to the original oxidation state of Cr. If the value of 9.8 × 10^{18} chromium ions to 1 m² of Cr_2O_3 (*14*) is taken into account, the amount of 0.09 ml O_2/m² corresponds to a change of the valency of Cr by one unit. The amount of oxygen adsorption established in our experiments corresponds approximately to a sorption of one oxygen atom to three surface molecules of Cr_2O_3.

C. Correlation between Structure and Activity of the Samples

Figure 3 shows the average adsorption data characterizing the structure of the model series of samples. The adsorption value for O_2 in ml/m² indicates to a first approximation the number of surface nickel atoms on 1 m² of the surface area of the sample (curve a), the value expressed in ml/g gives the total number of nickel surface atoms on 1 g of the sample (curve c). The

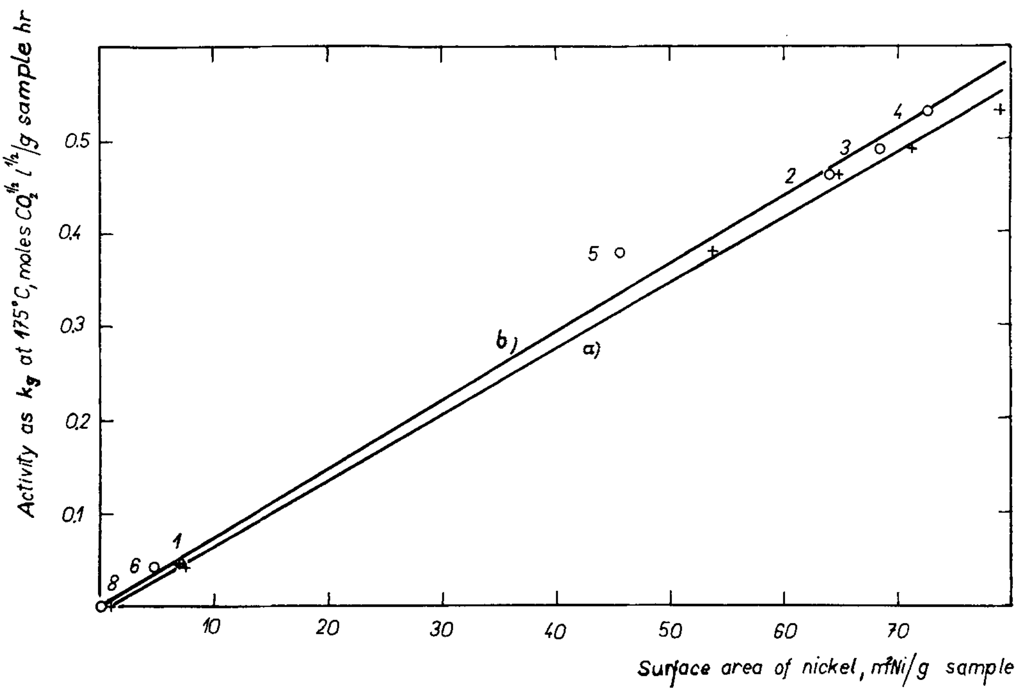

FIG. 4. Correlation between activity and surface area of nickel.

nitrogen adsorption data are expressed in the form of specific surface areas (curve b). For comparison the activities of the samples at 200°C expressed by the reaction rate constant related to 1 g of the reduced sample (curve d) are also presented.

Figure 3 demonstrates the following facts about the structure and activity of the samples: Nickel itself (Sample 1), though it has the largest number of Ni atoms on the surface area unit, is less active in the reaction, because the reduced sample has a small specific surface area. The original surface area of the unreduced sample 1 (NiO) is diminished from 121 m^2/g to 7 m^2/g due to recrystallization, occurring during the reduction. An addition of Cr_2O_3 to nickel stabilizes its structure, so that in spite of the decreasing number of Ni surface atoms on the unit of the surface area, the total number of Ni surface atoms on 1 g of the sample increases due to the enhancement of the specific surface area. The course of curve d demonstrates that the activity of the samples proceeds in a parallel dependence to the total number of Ni surface atoms. The best proof for this fact is demonstrated by the course of the dependences a to d between Samples 4 and 5, where the enhanced surface area does not succeed any more in compensating the reduction of the number of Ni surface atoms to 1 m^2, so that the total oxygen adsorption as well as the activity decreases. It follows from these results that the Cr_2O_3 is inactive in the given reaction and having, moreover, a comparatively small specific surface area it operates in the Ni catalysts as a typical structural promoter.

For further conclusions on the correlation between the oxygen adsorption and the activity, the ml O_2 NTP/g sample was recalculated for m^2 Ni/g sample. The following two procedures were used in these calculations.

(a) The adsorption of O_2 on Cr_2O_3 was neglected and the values were recalculated under the assumption of an identical adsorption mechanism of oxygen on Ni as well as on Ni/Cr_2O_3 catalytst. If a uniform distribution of the main three crystal faces of Ni is assumed and the extent of oxygen adsorption amounts to two layers, 0.555 ml O_2 NTP is adsorbed on 1 m^2 of nickel.

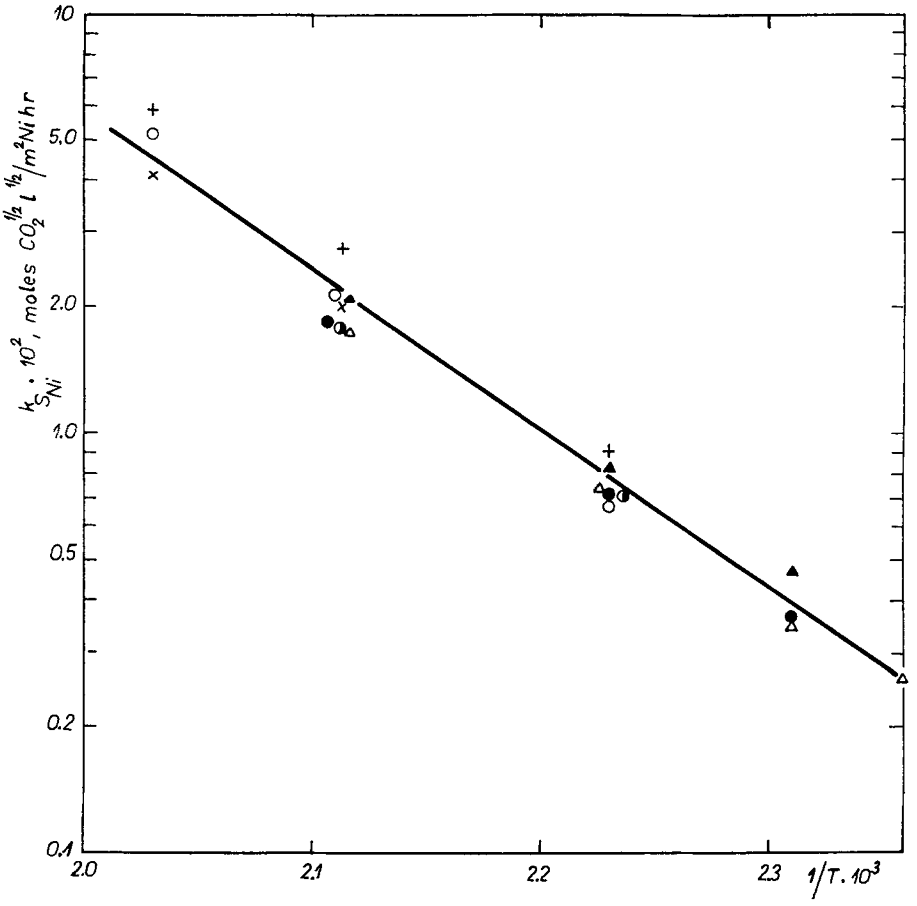

FIG. 5. Arrhenius plot for specific activities of nickel catalysts: ○, Sample 1; ●, Sample 2; ◑, Sample 3; △, sample 4; ▲, Sample 5; +, Sample 6; ×, Sample 7.

(b) Assuming that Ni and Cr_2O_3 show the same adsorption properties in an isolated state as in Ni/Cr_2O_3 catalysts, the following balance can be written:

$$S = S_{Ni} + S_{Cr_2O_3} \tag{3}$$

and

$$V = V_{Ni}S_{Ni} + V_{Cr_2O_3}S_{Cr_2O_3} \tag{4}$$

where S designates the total surface area of the samples in m^2/g; S_{Ni} is the Ni surface area in m^2/g sample; $S_{Cr_2O_3}$ is the surface area of Cr_2O_3 in m^2/g sample; V the oxygen adsorption in ml NTP/g sample; V_{Ni}, the oxygen adsorption on Ni alone in ml NTP/m^2 Ni; and $V_{Cr_2O_3}$ the oxygen adsorption on Cr_2O_3 alone in ml NTP/m^2 Cr_2O_3. The required value of the nickel surface area thus can be determined from the equation

$$S_{Ni} = \frac{V - V_{Cr_2O_3}S}{V_{Ni} - V_{Cr_2O_3}} \tag{5}$$

using the values for V and S measured on the separate samples and the value for $V_{Ni} = 0.555$ ml O_2 NTP/m^2 Ni and $V_{Cr_2O_3} =$ $= 0.024$ ml O_2 NTP/m^2 Cr_2O_3 measured on Samples 1 and 8.

The nickel surface areas calculated according to both procedures are listed in Table 1 and they are correlated with the activity of the samples in Fig. 4. The results obtained show that the activity of the samples is directly proportional to the nickel surface area and that neglecting of oxygen adsorption on Cr_2O_3 is tolerable in the given case

TABLE 1

COMPOSITION AND STRUCTURE OF SAMPLES

Sample	Composition molar ratio Ni:Cr_2O_3	Total surface area (m^2/g sample)	Surface area of Ni (m^2/g sample)	
			According to Procedure (a)	According to Procedure (b)
1	100% Ni	7.0	7.0	7.0
2	21.6:1	80.0	64.8	64.2
3	9.03:1	136.0	71.3	68.4
4	4.37:1	225.2	79.0	72.5
5	1.96:1	249.0	53.8	45.4
6	1:1.08	67.4	7.38	4.71
7	1:4.0	16.9	2.90	2.27
8	100% Cr_2O_3	19.0	0.83	0.0

TABLE 2

DATA ON ACTIVITY AND SPECIFIC ACTIVITY OF SAMPLES

Sample	Activity, k_g (moles $CO_2^{1/2}$ liter$^{1/2}$/g sample hr) at (°C):					Specific activity,[a] $ks_{Ni} \times 10^2$ (moles $CO_2^{1/2}$ liter$^{1/2}$/m^2 Ni hr) at (°C):				
	150°	160°	175°	200°	220°	150°	160°	175°	200°	220°
1	—	—	0.047	0.146	0.360	—	—	0.670	2.09	5.14
2	—	0.23	0.463	1.170	—	—	0.36	0.721	1.82	—
3	—	—	0.490	1.220	—	—	—	0.716	1.79	—
4	0.19	0.25	0.530	1.250	—	0.26	0.34	0.731	1.73	—
5	—	0.22	0.381	0.948	—	—	0.48	0.839	2.09	—
6	—	—	0.043	0.129	0.278	—	—	0.906	2.74	5.90
7	—	—	—	0.046	0.093	—	—	—	2.01	4.10
8	← Inactive →									

[a] S_{Ni} calculated according to procedure (b).

D. *Specific Catalytic Activity of Nickel*

Table 2 summarizes the data on the activities and the specific catalytic activities of the investigated samples. It follows from the table that while k_g values vary up to thirtyfold in dependence on the composition of the catalysts, the $k_{S_{Ni}}$ values change less than twofold only. Figure 5 shows that all samples can be represented in Arrhenius coordinates by one straight line the slope of which indicates the mean value of the apparent activation energy $E = 17.3$ kcal/mole. From the constancy of the specific catalytic activities of nickel in Ni catalysts promoted by Cr_2O_3 the conclusion can be drawn that only nickel represents their active component.

4. DISCUSSION

On the basis of the experimental results presented above not only the observation about the role of both components in Ni/Cr_2O_3 catalysts can be explained, but also further interesting conclusions can be drawn. It can be concluded from the constancy of specific catalytic activities and from the fact that the course of the reaction can be described on all samples by a single kinetic equation, that the reaction under investigation proceeds on all of the samples studied according to the same mechanism (it proceeds besides only on nickel). From the surface area of nickel in the sample its activity can be predicted in anticipation.

From a viewpoint of chemisorption methods for the determination of the surface area of metals the finding is also interesting, that the adsorption mechanism of oxygen on nickel does not depend on the presence of the oxide component. Another interesting point is the possibility of metal surface area determination according to Eq. (5), which has been derived assuming the adsorption on the oxide component of the catalyst. The data necessary for the calculations can be obtained by adsorption measurements on the studied catalyst and its isolated components. According to our knowledge (*1*) only cases of a completely selective adsorption on metals and the case of supported metals have been evaluated in the literature. In the latter case the adsorption on the support can be directly subtracted from the total adsorption, assuming that the surface area of the support and that of the catalyst prepared by its impregnation, are identical. The consistency of kinetics and adsorption data measured on the catalysts and their isolated components also indicates that the surface of Ni/Cr_2O_3 catalysts is probably composed of separate nickel and chromium(III) oxide crystallites.

A catalyst of the type Ni/Cr_2O_3 has been investigated from the viewpoint of its specific activity only by Soviet authors up to this day. In the work of Vlasenko *et al.* (*15*) one type of a catalyst was used and the total surface area as well as that of nickel was altered by sintering. The authors established the constancy of the specific activity measured at one temperature in the reaction of CO_2 hydrogenation to form CH_4. Ljubarskij *et al.* (*9, 10, 16*) used the hydrogenation of benzene as a model reaction and they found that the specific activity of Ni/Cr_2O_3 catalysts was the same as that of nickel powder as well as the catalysts Ni/MgO and Ni/carbon.*

Our results can be compared with those of other authors on the specific activity of metals in a series of other reactions. Platinum catalysts were, e.g., studied in the oxidation of sulfur dioxide and hydrogen and the hydrogenation of benzene and cyclopropane. The original papers of Boreskov *et al.* (*17–19*) as well as recent papers of the authors (*20, 21*) demonstrate that the impregnation of SiO_2 and Al_2O_3 with Pt does not alter its specific activity as compared with the "pure" metal, and that these supports have only a physical influence. A constancy of the specific activity was also found in various types of metallic nickel (powder, strip, plate, evaporated film, Raney Ni) in the hydrogenation of cyclohexene and ethylene (*22*) and the isotope exchange deuterium–hydrogen (*23*). Identical conclusions were drawn for more complicated nickel catalysts (Ni powder, Raney Ni, Ni/Al_2O_3, Ni/ZnO, Ni/asbest, Ni/SiO_2) in the hydrogenation of phenol (*24*) and the dehydrogenation of cyclohexane (*25*). These papers also indicate the inert character of the oxide components in the catalysts. On the other hand in a series of papers by Sinfelt *et al.* (*26–29*) a strong influence of the support on the specific catalytic activity of nickel and cobalt was found in the hydrogenolysis of ethane. The specific activity of Ni in Ni/SiO_2, Ni/Al_2O_3, and Ni/SiO_2-Al_2O_3 catalysts varied in its dependence on the type of support and metal content by up to four orders of magnitude (*29*). These findings could be interpreted either by the chemical interaction of the oxide with the metal, or by the fact that both components of the catalyst participate in the reaction. The conclusions about the specific activity of Fe in catalysts for the synthesis of ammonia are mutually not consistent (*30–32*).

A complex evaluation of the papers dealing with the specific catalytic activity is complicated by the fact that the samples used by various authors might not have the same structure and that the reliability of the method used for the determination of the metal surface area is not always guaranteed [see ref. (*1*)]. Now we would like to draw attention to the fact that various quantities are used for the expression of the activity. The use of the conversion stage (*25, 30, 33*) cannot lead to reliable results about the values of specific activities. The temperature dependence of the rate constant gives the best information. In this way it may be distinguished to what degree the catalytic activity of a surface of a solid substance is determined by the number of active surface sites on one hand and by their energetics (the intrinsic energy and possibly also the configurational energy which de-

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* Note added in the proof: Recently Mărgineanu, P., and Olariu, A., *J. Catalysis* **8,** 359 (1967) reported promoting action of chromia in a Ni/Cr_2O_3 catalysts for D_2/H_2O exchange reaction.

pends on the reaction mechanism) on the other. In other words, whether the catalysts compared differ only in the values of their frequency factor A in the Arrhenius equation, or also in the values of the activation energy E. The rate constants, however, can only be used if the reaction proceeds on the compared samples according to an identical kinetic equation. In the opposite case one must be satisfied with a comparison (at different temperatures) of the reaction rates at identical compositions of the reaction mixture.

Investigations on the specific catalytic activity have already contributed much information about the role of the oxide components in metal catalysts. The importance of this quantity however, must not be overestimated, as has been demonstrated by studies of the catalytic activity on oriented films and monocrystals. It might possibly be said that the expression of the activity of solid catalysts by their specific activity represents approximately the same progress in catalysis as the transition from the activity related to 1 g of the catalyst to the activity related to 1 m^2 of the total surface area.

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