

Increase of the Rate of Reduction of NiO by H₂, Due to Pretreatment with CO or NH₃

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When the reduction of pure NiO is initiated with CO or NH₃ at a sufficiently high temperature, an increase of the subsequent rate of reduction by H₂ in standard conditions is observed. This effect is larger than the increase of reducibility due to the addition of platinum. It arises from the formation of an increased number of nickel nuclei when NiO is treated with CO or NH₃. The pretreatment with NH₃ is preferably performed below 360°C, the Curie point of nickel. The rate of growth of the nickel nuclei in H₂ at 200°C is unchanged after a pretreatment with NH₃ or CO unless the latter is performed at 300-320°C (formation of Ni₃C) or above 390°C (formation of a rather large amount of free C).

INTRODUCTION

The reduction of pure and nonporous NiO by H₂ is a nucleation-growth process. This has been shown by the mathematical analysis of the reduction isotherms (1, 2) and by electron microscope examination (3, 4). A particle of NiO is reduced at only a few nucleation sites. The number of nickel nuclei and their rate of growth may be calculated by means of the theory of Mampel (5) improved by Delmon (1, 2).

It is well known that the presence of a metallic hydrogenation catalyst such as Pt or Pd on pure (6) or supported (7) NiO increases the reducibility, while Au and Ag have practically no effect in the same conditions. Other hydrogenation catalysts (molybdates, chromites) also increase the rate of reduction of pure NiO by H₂ (8). The formation of a larger number of nickel nuclei is invoked at the beginning of the reduction and ascribed to some activation of the H₂ molecule by the added compound. Several reviews about these effects and some related topics have been published recently (9, 10).

The positive effect of some transition metal carbides on the reducibility of NiO has been described and connected with the electronic properties of these additives (11). The nucleation step is also easier when modifying the energy spectrum of the NiO surface by means of a pretreatment with various salt solutions, e.g., KCl (12).

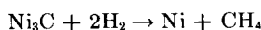
Since the NiO surface has a very low reactivity towards hydrogen, it may be profitable to form some nickel initially by an artificial method before the reduction by hydrogen. This was the case in the experiments performed by Delmon (13) where NiO was treated with formic acid, the small amount of Ni(HCOO)₂ formed being decomposed by heat treatment under vacuum just before the H₂ reduction experiment. A significant increase in the rate of reduction was observed in consequence of this HCOOH treatment. Similar observations have been recorded in this laboratory using the reducing power of the oil vapors from a greased-tap vacuum system (14), and of some hydrocarbons, e.g., *n*-butane (15) or *n*-hexane and cyclohexane (16).

This paper deals with the effect of a pre-treatment of NiO with CO or NH₃ and the subsequent reduction of this pretreated oxide by hydrogen.

METHODS

The same NiO as before (18), calcined in air at 950°C ($S = 1.1 \text{ m}^2/\text{g}$), is reduced in a McBain thermobalance. The slope of the quasi-linear region of the isotherm ($0.15 \leq \alpha \leq 0.5$) gives the apparent rate of reduction (k_e, min^{-1}) and its intersection with the time axis determines the induction period (t_i, min) (see Fig. 1).

When the reduction is completed in H₂, the degree of reduction ($0 \leq \alpha \leq 1$) is the ratio of the loss of weight at time t over the total loss of weight. A different method has been used to determine α_{CO} , because of the possible formation of Ni₃C and free C besides that of Ni. The free C does not react with H₂ below approximately 440°C (17). Moreover the weight change possibly due to



at 200°C may be neglected at least in a first approximation, since the amount of Ni₃C is very small under the present conditions. Therefore, the difference between the total losses of weight of NiO reduced

in H₂ at 200°C, untreated or treated by CO allows one to evaluate the degree of reduction of NiO by CO, α_{CO} ($0 \leq \alpha_{\text{CO}} \leq 1$). The wt% of free C may be obtained from the change of weight observed during the treatment by CO, corrected for the loss of weight due to the partial reduction of NiO by CO. The results are in fairly good agreement with those obtained by chemical microanalysis.

The water vapor (or CO₂) produced by reduction of NiO by H₂ (or CO) is trapped at liquid nitrogen temperature.

In the case of pre-reduction by NH₃, the trap is at -78°C (saturation pressure of NH₃ ~ 35 Torr). According to the good agreement between the losses of weight during the total reduction of NiO either by H₂ or by NH₃, only nickel and no nickel nitride is formed, in agreement with X-ray analysis.

After the pretreatment with CO (or NH₃) up to α_{CO} or α_{NH_3} values generally lower than 0.1, the reduction is always continued with H₂ in standard conditions ($T = 200^\circ\text{C}$, $p_{\text{H}_2} = 500 \text{ Torr}$). The values of k_e and t_i obtained in these conditions allow one to appreciate the efficiency of the pretreatment. In fact, the reduction by hydrogen at 200°C is used here as a "catalytic test reaction" for different samples.

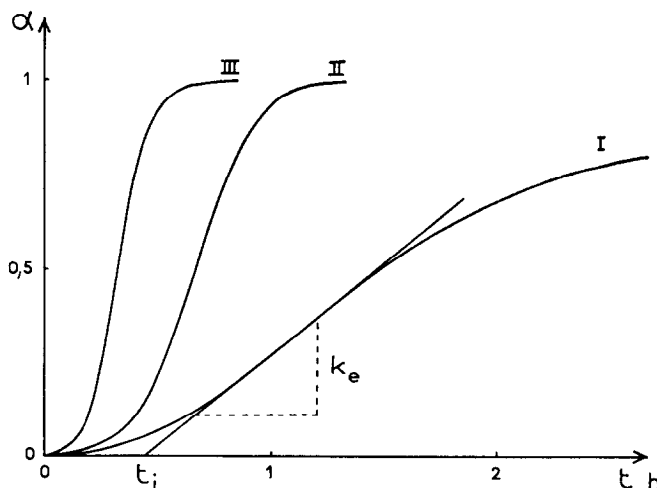


FIG. 1. Isotherms of reduction of NiO by H₂ at 200°C: (I) untreated, (II, III) after pretreatment with CO at 350°C [(II) $t = 20 \text{ min}$, (III) $t = 3 \text{ hr}$].

RESULTS

A. Pretreatments with CO

1. Influence of the Time of Treatment

($p_{\text{CO}} = 100$ Torr, $T = 350^\circ\text{C}$)

The sample ($m = 100$ mg) is outgassed during 15 hr at 200°C ($p = 3 \times 10^{-6}$ Torr) before introduction of CO. The temperature is subsequently increased to 350°C in 40 min. After heating for a time t at 350°C , the sample is cooled to 200°C in 30 min. CO is then evacuated and after a further 30 min vacuum treatment replaced by H_2 ($p = 500$ Torr).

Three isotherms of reduction are reported in Fig. 1. Figure 2 shows the variation of t_i , k_e , α_{CO} with t . The point ($t = 0$) is that of a sample just outgassed at 200°C . Curve III presents the course of reduction during the treatment with CO; curves I and II concern the reduction by hydrogen after the treatment. The wt% of free C increases from 0.15 for $t = 20$ min to 0.6 for $t = 5$ hr.

Figure 2 shows a large increase of the reducibility of NiO with respect to H_2 even for very low values of α_{CO} . The general variation of k_e (curve I) and α_{CO} (curve

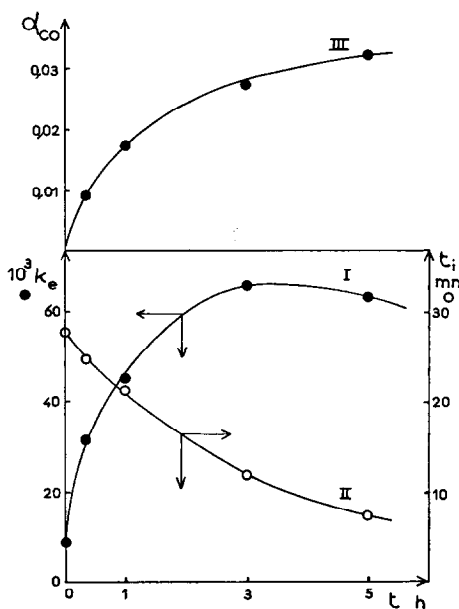


FIG. 2. Variations of k_e (I), t_i (II) and α_{CO} (III) with the time of treatment of NiO with CO at 350°C .

III) with the treatment time of NiO by CO is very similar. Curve III shows also that the reduction of NiO by CO at 350°C tends to stop when α is about 0.03 due to a self-poisoning reaction, presumably because some free C deposited on the solid builds a barrier between the reacting area and the gas phase.

2. Influence of the Temperature of

Treatment ($p_{\text{CO}} = 100$ Torr,

$t = 2.5$ hr)

The conditions are the same as before except that the time of outgassing of NiO at 200°C is 0.5 hr instead of 15 hr. This changes only slightly the reduction rate ($k_e = 7 \times 10^{-3}$ instead of 9×10^{-3} min^{-1}).

After a pretreatment of NiO with CO at 200°C , a large increase of t_i and a small increase of k_e are observed. This effect has been found to be less and less important when the temperature of treatment rises from 200 to 300°C .

Figure 3 shows the variation of k_e , t_i , α_{CO} and wt% C between 300 and 400°C . From the comparison of curves I (k_e), II (t_i) and III (α_{CO}), it appears that a value of

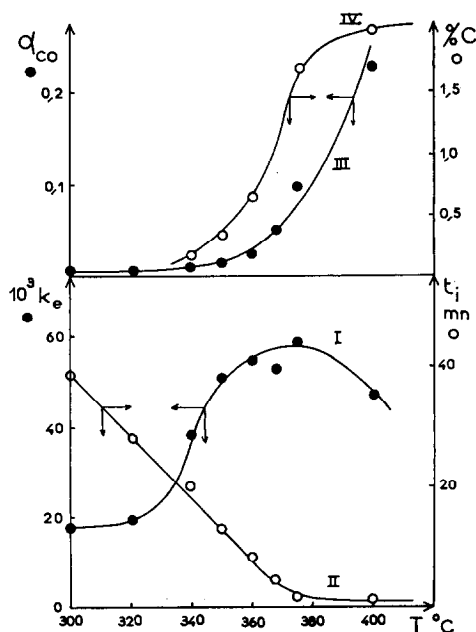


FIG. 3. Variation of k_e (I), t_i (II), α_{CO} (III) and wt% free C (IV) with the temperature of treatment of NiO with CO ($p_{\text{CO}} = 100$ Torr) ($t = 2.5$ hr).

α_{CO} of about 0.02 is sufficient to improve very markedly the kinetics of reduction of NiO by H_2 . Higher values of α_{CO} (up to 0.1 at 360–380°C) are not accompanied by a significant further increase of k_e and at the highest value of α_{CO} (0.2 at 400°C) a decrease of k_e is even observed. Curve IV shows that wt% of free carbon, like α_{CO} (curve III) begins to increase markedly from about 360°C, the Curie point of Ni. The rough similarity between curves III and IV is not surprising since the free carbon arises from the disproportionation of CO on Ni.

3. Influence of the Pressure of CO ($T = 350^\circ C$, $t = 2.5$ hr)

Figure 4 (curve I) shows that the value of $p_{CO} = 100$ Torr used in most experiments is, in practice, the optimum pressure condition. Moreover the variation of k_e (curve I) and α_{CO} (curve III) with p_{CO} is comparable, if one considers the low precision of the α_{CO} values which remain less than 0.02. It was not possible to determine the wt% of free C to a high accuracy for $p_{CO} > 100$ Torr because of disturbance in

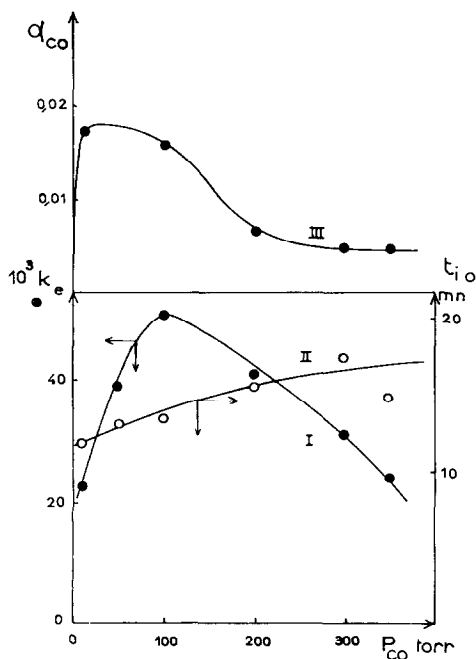


FIG. 4. Variation of k_e (I), t_i (II) and α_{CO} (III) with the pressure of CO ($T = 350^\circ C$, $t = 2.5$ hr).

the thermogravimetric measurements due to convection currents. The rate of formation of free C increases probably with p_{CO} and this free C is responsible for the self-poisoning of this reduction of NiO by CO.

B. Pretreatments with NH_3

NH_3 was purified by means of several condensation–evaporation cycles in liquid nitrogen traps. After outgassing 15 hr at 200°C ($p = 10^{-5}$ Torr) the sample was exposed to NH_3 ($p = 35$ Torr) at this temperature. The temperature was then increased in 50 min up to a definite value. At the end of the treatment, NH_3 was evacuated before cooling the sample to 200°C in 40 min. The interval of time between the stabilization of the temperature at 200°C and the introduction of H_2 is not of critical importance.

Two sets of experiments have been performed with various values of α_{NH_3} (Fig. 5). When the temperature is 320°C instead of 340°C, the reduction of NiO by NH_3 is very slow and the kinetics of the sub-

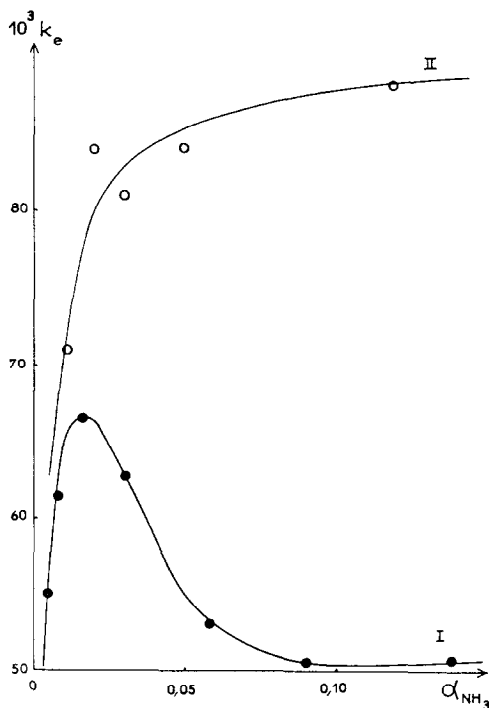


FIG. 5. Rates of reduction by H_2 at 200°C of NiO treated with NH_3 at 370°C (I) and 340°C (II).

sequent reduction NiO by H_2 is approximately the same as for the untreated NiO.

Figure 5 shows that, as with CO, the maximum value of k_e is attained when the value of α_{NH_3} increases to near 0.02. But while a further increase of α_{NH_3} does not very significantly change k_e at 340°C, a strong decrease of k_e is subsequently observed at 370°C (curve I).

The highest value of k_e after pretreatment with NH_3 ($85 \times 10^{-3} \text{ min}^{-1}$) is significantly larger than the optimum value observed with CO ($65 \times 10^{-3} \text{ min}^{-1}$) and is approximately tentimes the value of the blank NiO ($7 \text{ to } 9 \times 10^{-3} \text{ min}^{-1}$). For untreated NiO under the same conditions, the addition of 0.1 to 0.5% Pt increases the k_e value to $40 \times 10^{-3} \text{ min}^{-1}$ (12) which is significantly lower than the reduction rates obtained after the pretreatments described above.

C. Electron Microscope Observations

Electron microscopy has been performed at fixed values of α , after selective removal of the nickel phase with a Br_2-CH_3OH solution. In these conditions the unreduced parts of the NiO surface show a characteristic smooth appearance (3-4), while the reduced parts show a rough appearance. Generally speaking at $\alpha = 0.15$, the area of the unreacted parts of the NiO surface is smaller when k_e is larger.

In this way, a large number of electron microscope examinations have led to the following conclusions:

1. After a pretreatment of NiO with CO, a large part of the NiO surface is attacked; around the reduced areas some free C is observed;

2. During the pretreatment of NiO with NH_3 , almost the whole surface is involved in the reduction;

3. The interfacial area has a very different appearance after pretreatment with CO or NH_3 and after reduction by H_2 at 200°C. If after a pretreatment with CO or NH_3 , H_2 is admitted to the sample at 200°C, the interfacial area does not take immediately the appearance observed with NiO directly reduced by H_2 at this temperature.

DISCUSSION

The large increase of reducibility of NiO by H_2 is related to the formation of metallic nickel during the pretreatment with CO or NH_3 . Indeed, no increase of k_e and no decrease of t_i are simultaneously observed when the temperature is too low to allow formation of some Ni. Moreover, the formation of metallic nickel during pretreatments of NiO under vacuum (14) or with *n*-butane (15), *n*-hexane and cyclohexane (16) has been proved by thermomagnetic analysis. All these reducing species react with NiO in the same temperature range as CO or NH_3 and also give rise to an important increase of the subsequent rate of reduction by hydrogen.

According to the electron microscope observations the metallic nickel formed by reduction of NiO with CO or NH_3 is spread over a larger area of the NiO surface than the same amount of metal formed by reduction with H_2 at 200°C.

At least with CO, the Mampel-Delmon theory (1-2) leads to some conclusions which agree with the electron microscope observations. The experimental isotherms of reduction are drawn in the form $\omega = k\alpha/k_e = f(\alpha)$, where k_α is the instantaneous rate of reduction (min^{-1}) and $\alpha = \alpha_{CO} + \alpha_{H_2}$ or $\alpha_{NH_3} + \alpha_{H_2}$. They are compared to some theoretical curves drawn for various values of B_{S_i} (one quarter of the mean number of nickel nuclei per particle of oxide). Knowing B_{S_i} , it is possible to calculate k_i (cm min^{-1}) the linear rate of growth of the nuclei. It is assumed that:

1. All the nickel nuclei formed during the pretreatment are equal in size, and are larger than a certain critical size.

2. These nuclei are randomly distributed at the surface of NiO.

3. The number of new nuclei formed in H_2 at 200°C is negligible in comparison to the number of nuclei present after the pretreatment.

These hypotheses seem to be rather well fulfilled in the case of CO, accounting for the shape of the reduction isotherm of NiO by CO (Fig. 2, curve III) and con-

TABLE 1
REDUCTION OF NiO BY H₂, AFTER PRETREATMENT WITH CO

Treatment with CO			Reduction by H ₂ ($T = 200^\circ\text{C}$, $p = 500$ Torr)		
t (hr)	T ($^\circ\text{C}$)	α_{CO}	$10^3 \times k_e$ (min^{-1})	$4B_{S_i}$	$10^6 \times k_i$ (cm min^{-1})
0	350	0	9	— ^a	1.1
0.3	350	0.01	31.8	12	0.8
1	—	0.017	45.3	40	0.8
3	—	0.025	65.7	40	1.1
5	—	0.032	63.2	40	1.1
2.5	300	0.014	18.4	40	0.4
—	320	0.005	18.6	12	0.5
—	340	0.011	38.7	40	0.8
—	360	0.027	55.0	60	0.9
—	375	0.10	59.1	120	1.0
—	400	0.225	47.4	160	0.7

^a Not calculable because of a constant rate nucleation mechanism (18).

sidering the very low change of $4B_{S_i}$ with the CO treatment time (Table 1). Figure 6 shows the influence of the treatment temperature of NiO with CO on the value of $4B_{S_i}$. The activation energy is 18 kcal mole⁻¹ and the preexponential factor 8×10^7 . This value is approximately the same as the number of Ni²⁺ or O²⁻ surface sites present on a spherical particle of NiO of radius 0.45 μm (about 2.5×10^7). This is logical as the nucleation sites for the reduction of NiO by CO are chemisorption sites of CO on NiO. However, no CO chemisorbed on NiO at 200°C has been detected using a Sartorius microbalance (sensitivity 1 μg). But a value of $4B_{S_i}$ of, for example, 80 corresponds to about 3×10^{13} sites/g of NiO, that is $\approx 10^{-3}$ μg of CO chemisorbed, a value too low to be measured experimentally.

Table 1 also shows quite good agreement between the values of k_i obtained after the CO pretreatment and without it (18), except mainly at 300–320°C. In this temperature range the small amount of Ni formed by reduction of NiO with CO may be partially converted to Ni₃C (17). The slowing down of the interfacial rate of reduction of NiO by H₂ may be explained by the formation of traces of CO from Ni₃C in presence of H₂ (and H₂O) at 200°C. It has been found that the intro-

duction of CO ($p = 10$ Torr) in H₂ during the reduction of NiO by H₂ immediately stops the reaction, while in the same conditions CH₄ decreases the rate of reduction only by a half. Therefore, it is believed that traces of CO and CH₄ reduce k_i from 1.1×10^{-6} to 0.5×10^{-6} cm min⁻¹. A competitive chemisorption of CO with H₂ at the NiO–Ni interface explains the strong inhibition by CO.

In other respects, the electron microscope observations have also shown less roughness of the NiO–Ni interface after reduction with CO or NH₃, around 350°C than after reduction with H₂ at 200°C. When the reduction started with CO or NH₃ up to $\alpha \approx 0.02$ and then continued with H₂ at 200°C, the metal–oxide interface does not immediately recover the shape observed in the untreated NiO experiment (19). Since the linear rate of growth of the nickel nuclei $k_{i\alpha}$ is proportional to the value of the roughness degree of the NiO–Ni interface at a given degree of reduction α (18), it may be assumed that $k_{i\alpha}$ increases with α up to a constant value, k_i . This value (k_i , Table 1) would be attained once the interface morphology is the same in all samples, i.e., at $\alpha \approx 0.4$ as shown by the electron microscope observations. The mathematical analysis of the reduction curves is consistent with this model. The experimental

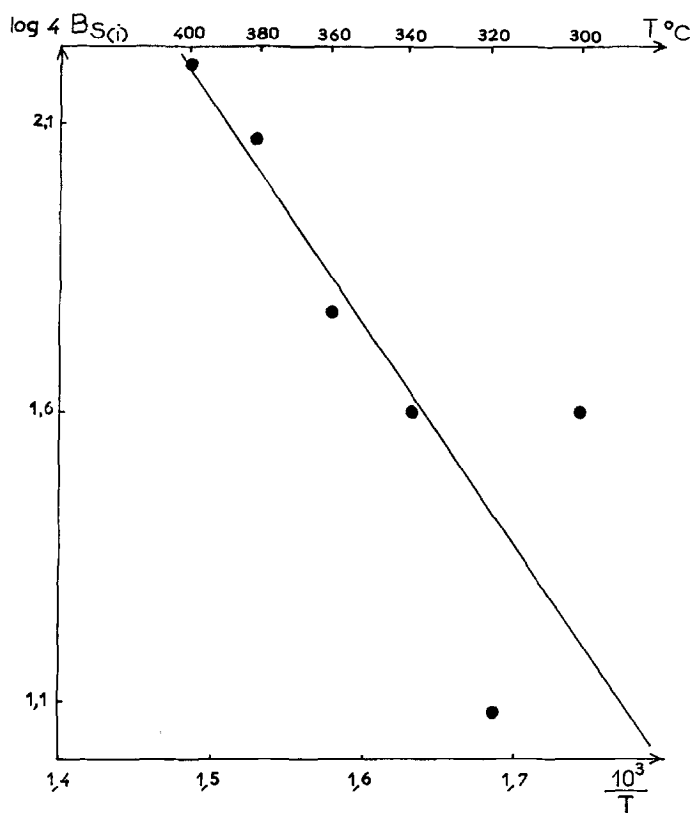


Fig. 6. Variation of $4B_{S(i)}$ (mean number of nickel nuclei per particle of NiO) with the temperature of treatment of NiO by CO.

$\omega = f(\alpha)$ curves of NiO pretreated with CO lie under the theoretical curves at $\alpha < 0.4$. The ratio of ω_{exp} over ω_{th} gives the ratio of $k_{i\alpha}$ over k_i . The variations of $k_{i\alpha}$ with α (Fig. 7) are in fact, very significant. Furthermore a progressive decrease of $k_{i\alpha}$ with α has been found for $\alpha > 0.7$. The same has been observed with the untreated NiO (18) and ascribed to an increased difficulty in diffusion of H_2 and H_2O to and from the interfacial area, when the unreduced NiO is coated by a rather large amount of Ni.

Concerning the pretreatment of NiO with NH_3 , a large difference is shown in Fig. 5 between this pretreatment being carried out below (curve II) or above (curve I) the Curie point of Ni (360°C). In the case of CO the effect of the magnetic transition is not so marked, probably because of the stabilization of the texture of Ni by free C. In fact, the difference between curves I

and II (Fig. 5) may be related to the sharp increase in the rate of sintering of Ni from 360°C , a phenomenon already described elsewhere (14). At 370°C the formation of new nickel nuclei and their disappearance by separation from the NiO surface act as competitive processes. The first prevails over the second for small treatment times (low values of α_{NH_3}). The reverse occurs gradually as the treatment time with NH_3 is increased in order to obtain higher values of α_{NH_3} , and hence the maximum in curve I.

A detailed mathematical analysis of the reduction isotherms obtained after pretreatment of NiO with NH_3 has not been possible. The condition I mentioned above does not hold for NH_3 because the reduction of NiO by NH_3 seems to occur with a constant rate of nucleation rather than with an instantaneous nucleation (20). Moreover, while a limiting size of the nickel nuclei is observed during the reduction of

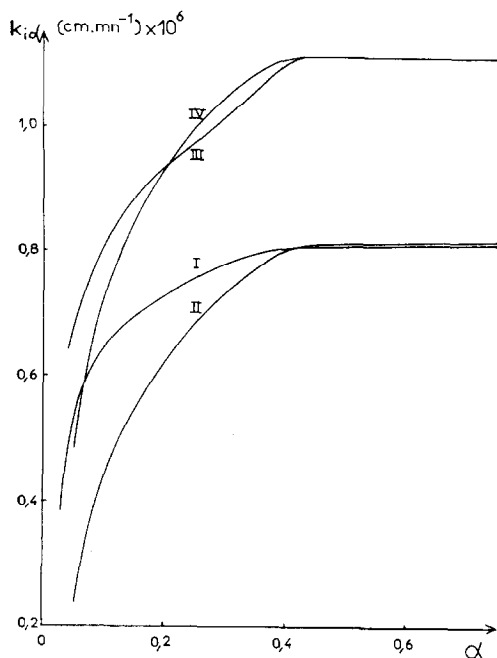


FIG. 7. Variation of $k_{i\alpha}$ with α , for NiO treated with CO at 350°C: 20 min (I), 1 hr (II), 3 hr (III), 5 hr (IV).

NiO by CO, it is no more the case with NH_3 since the reduction of NiO by NH_3 may be completed in the experimental conditions used (20). Since the NH_3 treatment leaves no residue in the sample a significant deviation of k_i in comparison to the value obtained for the untreated NiO ($\approx 1.1 \times 10^{-6} \text{ cm min}^{-1}$) is very improbable. The values of k_e obtained after the NH_3 pretreatment at 340°C ($\approx 85 \times 10^{-3} \text{ min}^{-1}$) are equal to the theoretical upper value of k_e calculable by the Mampel-Delmon theory for $k_i = 1.1 \times 10^{-6} \text{ cm min}^{-1}$. Consequently it does not seem possible to increase further the apparent rate of reduction of NiO by H_2 , without improving also the nickel nuclei growth step. A simultaneous increase of $4B_{S_i}$ and k_i has in fact been observed after pretreatments of NiO with hexanes (16). In spite of much work having been done dealing with the modifications of the number of nickel nuclei, much has still to be done about the possible modifications of their rate of growth.

As a conclusion, the theory of Mampel (5), as improved by Delmon (1, 2) and on a few points by the present authors (18),

has allowed several conclusions to be drawn which corroborate experimental or theoretical considerations. This theory gives a satisfactory fit of the kinetic measurements relative to the reduction of pure, powdered and nonporous NiO by H_2 .

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