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Promoter and Carrier Effects in the Reduction of NiO/SiO_2*

A. ROMAN** AND B. DELMON***

Institut Français du Pétrole, 92-Rueil-Malmaison, France

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The hydrogen reduction of nickel oxide deposited on silica is slow and incomplete, even at temperatures exceeding 400°C.

An anomaly in the plot of the rate of reduction versus temperature is observed at 375°C, where the rate passes through a slight maximum before regaining its regular increase, above 385°C. This anomaly could be related to the $\alpha \rightarrow \beta$ transition of nickel metal.

Platinum, palladium and copper promote the reduction to higher rates and a higher degree of transformation. Copper, introduced by reimpregnation of the catalyst, is the most efficient promoter and gains its full action for a proportion Cu/Ni less than 5%. The action of copper is comparatively more significant at lower temperatures.

Three types of nickel oxide can be discriminated in the silica supported catalysts, according to their reducibility. A first fraction, which is comparatively important at low NiO contents, is not reducible. It could be constituted of combined nickel oxide. The second fraction, which increases steeply with the NiO content, is spontaneously reducible. The third fraction is the "initiable" nickel oxide, whose reduction can be initiated by the promoter.

Two analogous mechanisms are proposed for explaining the variation of the proportions of spontaneously reducible and initiable nickel oxide with NiO content and temperature. Both mechanisms evoke nucleation inhibition as a consequence of the dispersion of nickel oxide. This inhibition could be caused either by the inability of nuclei to appear on layer domains which are too thin or by the absence of nucleus forming sites on some isolated domains. It is proposed that copper restores the nucleation ability of all domains.

This interpretation thus suggests that the inhibition of reaction caused by carriers can be explained, not only by the formation of chemical compounds with these carriers (which might be very important with alumina and silica–alumina), but also by the mere dispersion of the oxide.

INTRODUCTION

The so-called *activation* of supported nickel catalysts, i.e., the reduction of nickel oxide before the catalyst is put to work, is usually conducted at temperatures which are very high in comparison to those at which the reduction of bulk nickel oxide can be completed. It is a well-known fact that supported nickel oxide is much less reactive than when unsupported. The high reduction temperature promotes extensive sintering of nickel. It is thought that, in many instances, a better activity and/or a better poison capacity could be attained, if lower reduction temperatures could be used. Furthermore, a regeneration of nickel catalysts, which is usually not attractive, could become so, if a means could be found to prevent sintering of nickel in the regenerated product.

In conformity with the experience of

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* This publication is part of the doctoral thesis by A. Roman.

** Present address: Battelle, Geneva Research Center, 1227-Carouge, Switzerland.

*** Université de Louvain, Kardinaal Mercierlaan 92, 3030-Heverlee, Belgium.

people concerned with catalyst manufacture, recent publications suggest that various promoters of nickel catalysts are effective, not because of some modification of the catalytic properties, but as a consequence of a better activation or regeneration. This effect would be similar to the initiating action of various metals like copper, cobalt, palladium or platinum on the reduction of the unsupported oxide (*1–6*). Nowak and Koros suggested this explanation for the increased hydrogenolysis activity of nickel catalysts containing a small amount of platinum or palladium (*7*, *8*). Cosyns, Chênebaux and Miquel proved (*9*) that there was a direct correlation between the hydrogenating activity of silica or alumina supported catalysts and the quantity of nickel which was reduced during the activation. They showed that the addition of small amounts of copper increased the proportion of reduced nickel.

The reduction kinetics of supported nickel oxide have been studied by various authors (*7*, *10–15*). The results presented here contribute to give additional insight into the mechanism, thanks to the analysis of the effects of foreign metal (i.e., copper) additions.

METHODS

Silica is known to be the carrier which imparts the best hydrogenating activity to nickel (*14*). All our samples were supported on silica. The silica, supplied by Procatalyse, had the following characteristics: Specific surface area, 334 $m^2\ g^{-1}$; total pore vol, 0.92 $cm^3\ g^{-1}$; mean pore diam, 110 Å; Na content, 0.22% wt. The carrier was crushed, and only particles of diameter between 100 and 250 μm were used.

Impregnation is known to give samples having an activity, with respect to hydrogen, which is higher than in those obtained by coprecipitation (*16*). We therefore resorted to impregnation. The particles were impregnated with a solution of nickel nitrate of a volume equal to the total pore volume. The powder was subsequently dried under vacuum, at 110°C, for 4 hr, and calcined in air.

Most experiments were carried out on a catalyst containing 18.9% wt Ni, calcined at 500°C in air, for 5 hr. Other Ni contents, as well as other calcination temperatures, were occasionally used.

The addition of foreign substances (in most instances, copper) was made by a second impregnation with a volume of a solution of the metal salt or salts equal to the pore volume of the catalyst. Copper, palladium, cobalt, zinc and lithium were introduced as nitrates, molybdenum and tungsten as, respectively, ammonium paramolybdate or metatungstate, and platinum as hexachloroplatinic acid. The reimpregnated samples were subsequently calcined at 500°C, in air, for 5 hr.

X-Ray diffraction data indicated that the supported nickel oxide was well crystallized. No compound formed with silica was detected. No detectable shift of the X-ray lines was observed. The standard catalyst (18.9% wt Ni) had a specific surface area of 250 $m^2\ g^{-1}$.

The hydrogen used for reduction was passed through a Deoxo device and a liquid nitrogen trap.

The reduction was carried out in a recirculation apparatus, with a shuttled reactor. The apparatus is an improved model (*17*) of a device which has already been described (*4*, *18*). Many studies have shown that, provided the particles of reactant have a diameter lower than 500 μm, this type of apparatus yields results which are practically not impaired by diffusion limitations (*4*). The reaction was measured by the fall in hydrogen pressure, initially 760 mm Hg. Complete reduction at 325°C of a standard 4 g sample containing 18.9% Ni corresponded to a pressure drop of 320 mm Hg.

RESULTS

I. General Observations

The degree of reduction, α, of NiO/SiO_2 has been plotted, in Fig. 1, as a function of time, for various temperatures (*19*). The reaction is much slower than with unsupported NiO and apparently never goes to completion. In addition, the curves do not exhibit (*12*) the S shape observed with pure

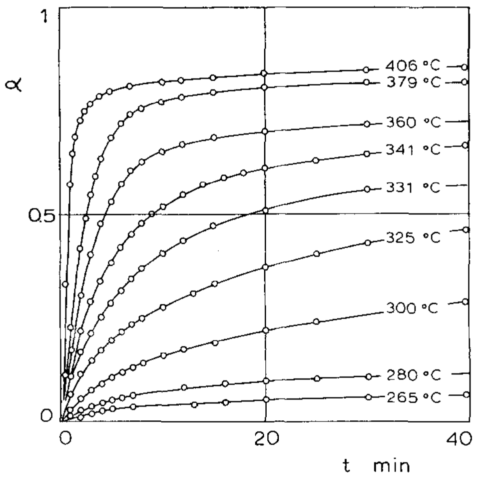

FIG. 1. Reduction-time curves of NiO/SiO_2 at various temperatures.

NiO. Although the supported oxide was calcined at a much lower temperature (500°C) than the unsupported one (900°C), and is presumably more dispersed (the specific surface area of the unsupported oxide was only 1.6 m^2 g^{-1}), it reacts much more slowly. At 265°C, for example, the unsupported oxide was completely reduced in 40 min, whereas only 7% of the supported oxide was reduced during the same time.

The influence of the *calcination temperature* of the supported sample on the reduction kinetics has been investigated (Fig. 2). The reduction kinetics can be characterized by $t_{0.25}$, which is the time necessary for 25% NiO to be reduced, and α_{max}, which is the maximum degree of reduction apparently obtained (after 3 hr). Figure 2 shows that the optimum calcination temperature is 400–500°C. Our standard samples were prepared at 500°C. After a calcination at 800°C, NiO is very poorly reactive. When the calcination temperature is too low, the reactivity is also low, probably because of an incomplete decomposition of the nitrate ions (*20*).

The influence of temperature on the *reduction* process is represented in Fig. 3. This figure is an Arrhenius plot of the inverse of $t_{0.25}$ and $t_{0.50}$ (times necessary to attain, respectively, 25 and 50% reduction). An irregularity shows up at 375°C. This irregularity is discussed below.

II. Effect of Various Treatments

The catalyst samples were subjected to various treatments which had proved effective in promoting the reduction of the unsupported NiO.

Impregnation with formic acid, followed by decomposition under vacuum of the superficial formate formed by this process, causes a strong acceleration (by a factor of 3) of the reduction of the unsupported oxide (*4*, *18*, *21*). This acceleration can be explained by the presence of nickel nuclei, produced by the decomposition of the surface formate. These nuclei initiate the reduction. The acceleratory effect turns out to be much less important with the supported oxide, as indicated by Table 1, where the respective ratios between the quantities $t_{0.25}$, $t_{0.50}$ and α_{max}, for treated catalysts and those for untreated catalysts have been calculated.

The effects of various metal modifiers on

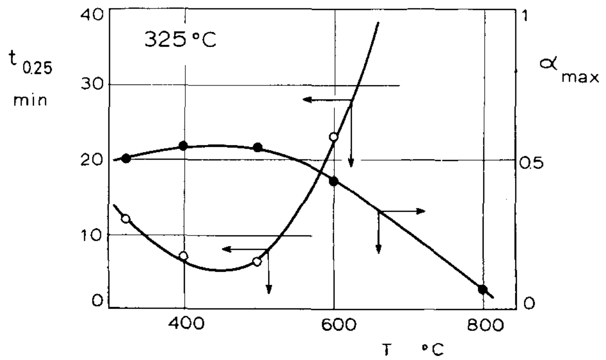

FIG. 2. Influence of the calcination temperature on the reduction kinetics of NiO/SiO_2 (325°C).

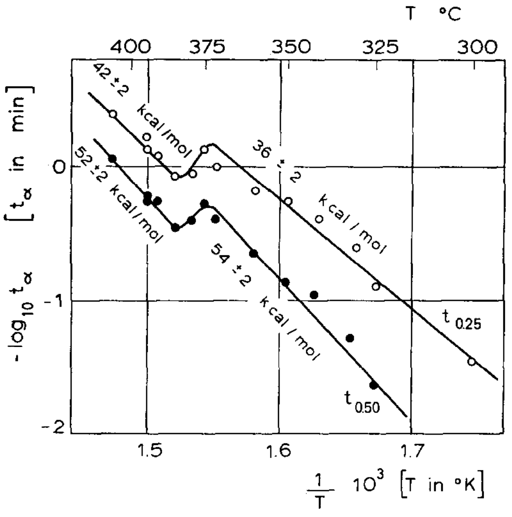

FIG. 3. Influence of the temperature on the rate of reduction of NiO/SiO_2.

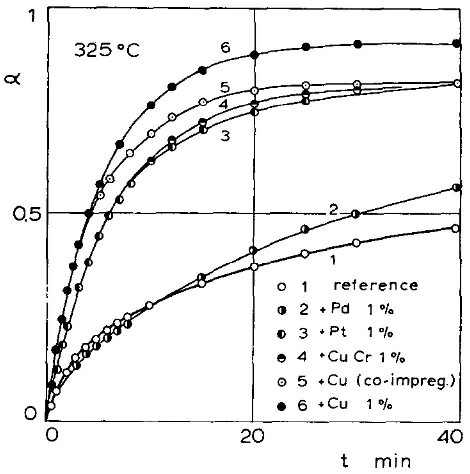

FIG. 4. Effect of various promoters on the reduction-time curves of NiO/SiO_2 (325°C).

the reduction of supported oxide at 325°C have been investigated. The modifiers were added by the reimpregnation technique indicated previously. The quantity introduced was 1% wt (as metal) in the catalyst (containing 18.9% Ni), i.e., 5.3% wt respective to nickel. The following modifiers had an inhibitory action: WO_3, ZnO, $CoMoO_4$, MoO_3, Li_2O and Cr_2O_3 (in order of increasing effect). The effect of the modifiers which had been proved to have an acceleratory action on the reduction of the unsupported oxide (*1–6*) is indicated in Fig. 4. Cobalt has practically no effect and palladium only a slight acceleratory one. Platinum, copper chromite and, chiefly, copper, have a considerable promoting effect. Similar results were obtained at 280°C.

Because of the intensity of the acceleratory action of copper, all subsequent experiments were made with this metal as initiator.

III. Promoting Action of Copper

Curves 6 and 5 in Fig. 4 corespond, respectively, to a sample which was reimpregnated according to the standard procedure and to a sample where nickel and copper nitrate were deposited *simultaneously* (co-impregnation). Co-impregnation gives substantially less reactive samples than reimpregnation.

The influence of the amount of copper, introduced by reimpregnation, on the reduction kinetics of supported nickel oxide is indicated by the results of Table 2, where the ratios $t_{0.25}$, $t_{0.50}$ and $\alpha_{\max}$ to the corresponding values obtained with a catalyst without copper are shown. Copper in excess of 0.5% wt with respect to the

TABLE 1

ACTION OF A TREATMENT WITH FORMIC ACID ON THE REDUCIBILITY OF NiO/SiO_2 (18.9% wt Ni)

Treatment	Reduction *T* (°C)	$t_{0.25}$ (min)	$t_{0.50}$ (min)	$\alpha_{\max}$ (3 hr)	$\frac{t_{0.25\,(\mathrm{ref})}}{t_{0.25}}$	$\frac{t_{0.50\,(\mathrm{ref})}}{t_{0.50}}$	$\frac{\alpha_{\max}}{\alpha_{\max\,(\mathrm{ref})}}$
None (reference)	280	∞	∞	0.115	—	—	1
Formic acid, 10%	280	∞	∞	0.15	—	—	1.30
None (reference)	325	8	56	0.54	1	1	1
Formic acid, 10%	325	6	35	0.56	1.33	1.70	1.04
Formic acid, 98%	325	6.8	36	0.58	1.18	1.56	1.07

TABLE 2

INFLUENCE OF COPPER ON THE REDUCTION OF NiO/SiO_2 (18.9% wt Ni) (325°C)[a]

$\frac{Cu}{NiO + SiO_2}$ (%)	$t_{0.25}$ (min)	$t_{0.50}$ (min)	α_{max} (3 hr)	$\frac{t_{0.25\ (ref)}}{t_{0.25}}$	$\frac{t_{0.50\ (ref)}}{t_{0.50}}$	$\frac{\alpha_{max}}{\alpha_{max\ (ref)}}$
0	8	56	54	1	1	1
0.33	2.2	5.7	91	3.6	9.8	1.68
0.50	1.6	4.0	93	5	14.0	1.72
1.00	1.6	4.0	93	5	14.0	1.72

[a] The amount of copper is expressed as metal weight over total catalyst weight.

total sample has practically no additional promoting effect.

DISCUSSION

Carriers have many distinct functions in improving the quality of catalysts. They enable a better dispersion of the supported active agent and prevent to a great extent its sintering at higher temperatures. They sometimes possess their own catalytic activity, which implements the overall efficiency of the catalyst. They also modify many properties of the deposited substance, an effect which may be either favorable or deleterious. The results reported above are discussed in relation with the possible effects that a carrier may exert on the deposited substance.

We first discuss the anomaly in reactivity observed near 375°C (Fig. 3). A maximum in reduction velocity is observed near 375°C. The rate of reduction (expressed as the inverse of $t_{0.25}$ or $t_{0.50}$) decreases for temperatures slightly higher, and only recovers its 375°C value near 385°C.

This anomaly has some analogy with the reactivity maximum which was observed with the unsupported oxide near 265°C (*22–24*), and which was shown to be related to the Néel transition of nickel oxide. However, the Néel transition of the supported oxide is unmodified and remains at 265°C, as indicated by the specific heat anomaly detected by differential thermal analysis (in air). No effect is observed near 375°C.

Reactivity anomalies of nickel containing compounds near 375°C have been observed by Nury and Forestier (*22*), and by Keely and Maynor (*20*). The former authors mentioned a maximum in the reactivity of unsupported nickel oxide with hydrogen near 350°C, and related this effect to the Curie point of nickel. The latter studied the decomposition of nickel nitrate by differential thermal analysis and found a small endothermic effect at 360°C, which was interpreted to be caused by the $\alpha \rightarrow \beta$ transition of nickel. Such an explanation implied that a small quantity of nickel was formed during the decomposition of the nitrate.

We are thus led to suppose that the anomaly in the reactivity of the supported oxide near 375°C could be related to the $\alpha \rightarrow \beta$ transition of nickel and that it has no relation with the presence of the carrier. Concerning the Néel transition near 265°C, no equivalent of the effects observed with unsupported oxide can be detected because of the extremely low reactivity of the supported oxide at this temperature.

We shall now examine the other effects which have been reported above, and which can all be related to some action of the carrier.

The main effects of the silica carrier are to reduce strongly the reactivity of nickel oxide and to inhibit its complete reduction. The amount of nickel which can be reduced before attaining the apparent reduction limit indicated by the pseudo-asymptotes on Fig. 1 depends on the reduction temperature. Fig. 5 (*19*) is a plot of this apparent reduction maximum as a function of temperature. It seems that, above 380°C, very little is gained, and the illustration suggests that it is practically impossible to reduce more than 90% of the oxide, even

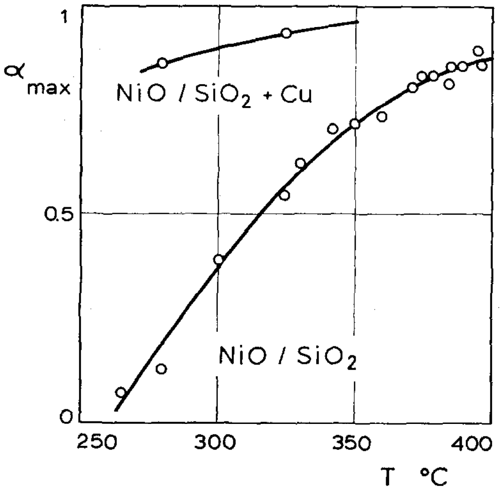

FIG. 5. Apparent maximum α_{max} of the degree of reduction versus temperature, for pure and promoted NiO/SiO$_2$.

at temperatures higher than 400°C and for very long reaction times. The literature indicates that nickel oxide is still less reactive when deposited on alumina or silica-alumina (*11*, *12*, *14*).

This inhibiting effect of the carrier cannot be ascribed solely to diffusion limitations impeding the access of hydrogen to nickel. The best proof lies in the strong acceleratory effect of some foreign metals. Figure 4 shows that reaction rates 2–5 times more rapid can be attained, although the texture of the catalyst is unchanged. The difference in the inhibitory effect according to the chemical nature of carriers suggests some specific action of the latter. This effect, however, does not seem to be related to any difference in structure of nickel oxide, as supported NiO exhibits normal X-ray and DTA diagrams.

Moreover, the formation of chemical compounds of nickel oxide with silica, if any, is certainly very limited. X-Ray analysis reveals neither new phases nor any displacement of the lines of NiO. This holds true even for a supported oxide prepared at 800°C, although the latter has a very low reactivity.

One is thus led to assume that, although the deposited species is substantially pure nickel oxide, the presence of the carrier induces large differences in reactivity between different parts of the supported oxide. The presence of some foreign metals, like copper, promotes the reduction of some parts of nickel oxide, which would otherwise remain unreacted. Figure 5, where the apparent maximum degree of reduction of copper-promoted samples at 280 and 325°C has been indicated, suggests that the proportion of otherwise inactive oxide which can be promoted by copper is comparatively higher at a lower temperature.

It is convenient to distinguish between three parts of nickel oxide, according to their reaction ability at a given temperature. The first part will be called *spontaneously reducible*. It is the part which reacts in unpromoted samples. The second part, which is reduced in the presence of the most effective promoter, namely copper, will be called the *initiable* nickel oxide. The third part will be labeled *unreducible*.

We have determined these three parts in a series of four samples with various NiO contents, pure or promoted with the same proportion (respective to nickel) of copper, i.e., Cu/Ni = 5.3%. The experiments were conducted at 325°C. Figure 6 sums up the results.

Figure 6 suggests that the amount of unreducible nickel oxide varies only slightly with the total nickel oxide content. At very low contents, most of the nickel oxide seems to be withdrawn from reduction.

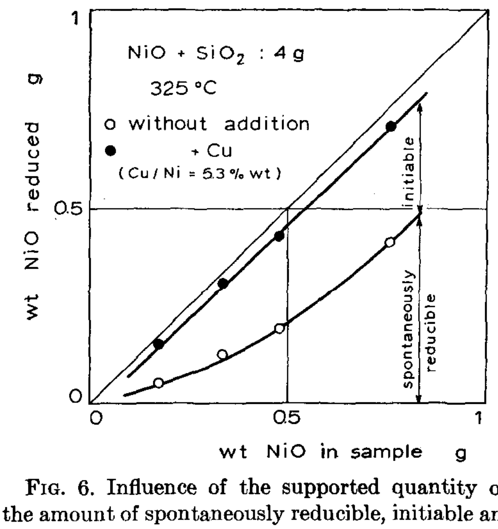

FIG. 6. Influence of the supported quantity on the amount of spontaneously reducible, initiable and unreducible NiO at 325°C.

We have insufficient results to discuss the possible nature of the unreducible part of nickel oxide. It might be constituted of a small quantity of a hypothetical silicate compound. From electron diffraction and nickel extraction studies, Coenen and Linsen (*25*) found indications that some nickel antigorite is present in their supported nickel samples, with high nickel contents, which had been prepared by precipitation. Formation of nickel antigorite, however, occurs only to a very limited extent at lower nickel contents (20%), and there is no indication in the literature of the presence of silicate compounds in impregnated samples. Another explanation for the unreducible part would be that it corresponds to portions of nickel oxide which are nearly completely encapsulated in the carrier (in narrow neck pores).

Our discussion will concern the reasons which could explain the small reactivity of the supported oxide, together with the variation of the proportion of spontaneously reducible and initiable nickel oxide as a function of deposited quantity and temperature. As this discussion has to take into account the modifications of reactivity observed after a treatment by foreign substances, it is convenient, beforehand, to examine the possible mechanisms of action of such foreign substances.

The results obtained in recent years in the reduction of unsupported oxides (mainly nickel oxide) suggest that several mechanisms can probably explain the effect of various surface treatments or additives on the reactivity.

It was initially thought that the acceleratory action of platinum, palladium, copper and cobalt could be explained by the easier formation of metal nuclei, because of the ability of these metals to activate hydrogen (*1, 2, 4*). In this interpretation, the foreign metals are thought to play somehow the same role as the nuclei of the reduced metal. The similarity of the effects observed with artificial nickel nuclei and with foreign metals in the reduction of nickel oxide was a strong argument supporting this view (*2, 4*).

The fact that pure foreign metals in powder form, simply admixed with nickel oxide, acted as activators (*1, 2*) indicated that no modification of the oxide surface structure was involved in the reactivity modifications. This view was further supported by experiments showing the acceleratory action of hydrogen activating catalysts (e.g., supported palladium or platinum) when also admixed with the reactant (*5*). In the latter experiments, the mere activation of hydrogen (together with spillover and jumpover processes) was emphasized.

But other experiments indicate that the modifications of the surface of the oxide reactant by ion exchange during the surface treatment also considerably alter the reactivity (*6*). It seems that the mere exchange of metal ions, e.g., nickel on the surface of the oxide, with other ions which are either more easily or more difficultly reducible, readily explains, respectively, the increase or the decrease of reducibility of the oxide. In addition, some anions can also modify the reactivity (*8, 26, 27*).

The inhibitory action of WO_3, ZnO, $CoMoO_4$, MoO_3, Li_2O and Cr_2O_3 in our experiments could probably be related to this second sort of effect, namely ion exchange. The acceleratory action of copper, platinum and palladium is consistent with all previous results (*1–3, 6–9*), but its interpretation is less straightforward. The effect of a treatment with palladium, for example, is much less important than reported previously (*6–8*). It was emphasized that the chlorine ion plays a special role in the case of palladium (*8*). Our results might be explained by the fact that palladium was introduced as nitrate, instead of chloride. Concerning the strong acceleratory action of copper, which has consistently been observed by various investigators, two different interpretations were proposed. This action could be related to the formation of a solid solution of copper oxide in the outermost layers of nickel oxide. Such solid solutions have been shown to reduce more easily than pure nickel oxide (*28, 29*). The acceleratory effects could also be attributed to the presence of copper aggregates on top of the nickel oxide layers, with copper acting by mere contact, like pure or supported palladium or platinum (*1*, *5*).

We now come to the discussion of the influence of the carrier in the reduction of supported nickel oxide. The mechanisms which will be proposed do not depend on the exact process by which copper promotes this reduction. In our representation, the only important fact is that copper enables all nickel oxide, except the unreducible part, to react. This can be accomplished either by some ion exchange between nickel and copper during the reimpregnation and the subsequent calcination, which produces a more easily reducible superficial solid solution, or by the formation of small copper aggregates acting as nuclei on the surface of nickel oxide.

Concerning the influence of the carrier on the reduction of supported nickel oxide, the important facts are the increase of the proportion of spontaneously reducible nickel oxide with temperature and with the NiO content of the catalyst. Two mechanisms can be proposed to explain these facts.

The first one takes into account the *thinness* of the nickel oxide layers on silica (Fig. 7a). It is known that a nucleus of a new phase has a critical minimum size below which it is unstable and actually does not appear. The hypothesis is that spontaneous nuclei could not form on layers which are too thin. The fact that the formic acid treatment, which is highly effective with unsupported nickel oxide, has practically no effect with supported samples, is a good indication in favor of this hypothesis. Accordingly, only the aggregates with portions of sufficient thickness could nucleate. Because of the discontinuities of the deposited oxide, the aggregates with insufficient thickness would never be in contact with growing nuclei and would therefore remain unreacted. Copper could activate practically all the reducible nickel oxide, either by reducing the minimum size requirements for stable nuclei, or by inducing reduction without the necessity of forming nuclei. This explanation accounts for the incomplete spontaneous reduction. It also accounts for the increase of the spontaneously reducible

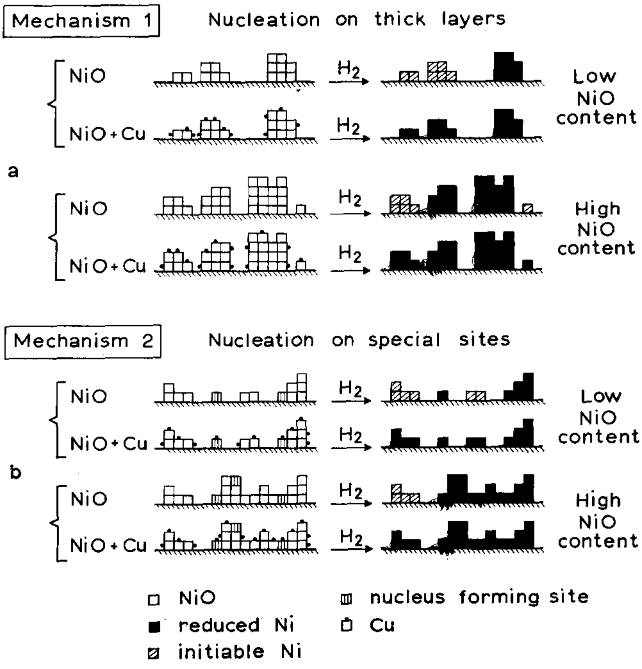

FIG. 7. Schematic representations of mechanisms for the reduction of supported nickel oxide.

proportion of nickel oxide with NiO content, because of thicker layers. The increase of spontaneous reducibility with temperature would be explained by easier nucleation (i.e., nucleation on thinner layers), as it was demonstrated on unsupported nickel oxide that the rate of nickel nucleation increases very rapidly, particularly above 265°C, where a nucleation activation energy of about 45 kcal mol^{-1} is measured (*24*).

According to a second explanation (Fig. 7b), one could assume spontaneous nucleation to be possible only at *special nucleus forming sites* (special crystal defects, for example), which would be present at certain places *irrespective of layer thickness*. As in the previous explanation, because of the highly dispersed, patchlike, distribution of nickel oxide at low NiO contents, patches, where no sites of spontaneous nucleation are available, would remain unreacted. On the other hand, at high NiO contents, as a consequence of more contacts between patches, reduction could propagate easily to other domains from sites where spontaneous nuclei form. As in the former explanation, the role of copper as well as that of an increased temperature would be to make uniform the possibility of nucleation all over the surface.

The former explanation seems to be substantiated by Alais (*30*), who, by studying the reduction of partially reoxidized coprecipitated nickel–silica catalysts, shows that the reaction cannot propagate across discontinuities and is restricted to the biggest nickel oxide particles.

Both proposed mechanisms take into account nucleation effects. It might be argued that the reaction does not exhibit the S-shaped reduction versus time curves characteristic of nucleation limited phenomena. Actually, this degeneracy to kinetics characterized by regularly decreasing velocity is also always observed with the unsupported oxide, when the latter is highly dispersed, although all authors now agree that the reduction of nickel oxide is nucleation limited (*4*). An additional argument in favor of nucleation is that the effects observed in the partial reduction of supported MoO_3 to Mo^{5+} species can only be explained by a mechanism closely resembling the first one presented above (*31, 32*).

Neither mechanism readily explains the decrease of the proportion of spontaneously reducible nickel oxide in samples calcined at temperatures above 600°C (Fig. 2). An increased calcination temperature would promote the formation of thicker nickel oxide aggregates. This would probably diminish the number of contacts between aggregates by promoting the diffusion of nickel oxide from interconnecting "isthmuses" to thicker domains. It would also diminish the number of potential nucleus forming sites. The first effect would cause an increase of the spontaneous reducibility, whereas the last two would have the reverse influence. A complete interpretation of the effects observed with samples calcined above 600°C would thus necessitate additional investigations, with respect to the textural distribution of nickel oxide on the carrier.

CONCLUSION

The fact that supported oxides are more difficultly reduced than unsupported ones has often been attributed to the formation of chemical compounds with the carrier. In the case of nickel oxide, this probably explains why the reactivity is lower when the oxide is deposited on alumina or silica–alumina rather than on silica. The formation of a chemical compound with silica could also account for the small amount of "unreducible" nickel oxide. But silica is relatively inert to nickel oxide. The variations of the proportion of spontaneously reducible nickel oxide with temperature, together with the activating effect of foreign metals, suggest that the lower reduction rates observed with the supported oxide may be principally attributed to dispersion and to the smallness of the crystallites.

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