Increase of Reducibility of NiO by H$_2$, Due to Pretreatment with Salt Solutions

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The impregnation of a high temperature preparation of pure NiO with various salt solutions, followed by drying and extraction with water, affects the reducibility of NiO differently according to the nature of the cation. Whereas no positive effect is observed with Li, Cs, Zn, Cd, Hg, Al, La, Fe, or Co, the rate of reduction in dry hydrogen becomes about twice as much that of the starting NiO for Na, K, Rb, Mg, Sr, Ba, Au, and Ni. This is ascribed to the formation of some disordered superficial areas on NiO. More pronounced effects occur with Cu, Pt, Pd, Ru, Rh, Os, Ir, and are related to a cationic exchange with surface Ni^{2+} during impregnation. The effect of most Group VIIIa elements changes with the percentage of d character of the metallic bond as does the specific catalytic activity in some particular reactions. A large difference of the thermal stability of artificial nucleation areas formed during the considered treatments is evidenced. From this point of view Pt is much more favorable than Os. Finally, the fraction of platinum which is extractable by water after impregnation of NiO with H$_2$PtCl$_6$ or Pt(NH$_3$)$_2$(NO$_2$)$_2$ gives rise to a metallic phase which increases the rate of reduction only slightly.

INTRODUCTION

The increase of reducibility of various pure or supported metallic oxides in the presence of Pt or Pd has recently received considerable attention. For instance, the catalysis of hydrogen uptake of WO$_3$ by Pt, evidenced by Khoobiar (1) and precisely stated by Benson, Kohn, and Boudart (2) is a well known phenomenon. Elsewhere, Verhoeven and Delmon (3) have indicated the efficiency of Cu, Pd, and Pt in the reduction of pure NiO, while Au and Ag are apparently ineffective. Similar conclusions about the difference of behavior of Pt, Pd, and of Au–Ag have been reported by Nowak (4) for NiO supported on alumina. Chenebaux, Cosyns, and Miquel (5) have investigated the catalysis of the reduction of supported NiO by means of copper. The positive effect of Pt and Pd on the reduction of supported iron oxide has been studied by Sancier and Inami (6) by EPR.

Hydrogen is assumed to be possibly activated by the foreign metal into a form which is more or less similar to atomic hydrogen and which migrates to the oxide. This is partly confirmed by some results about hydrogenative properties of Pt–SiO$_2$ (7) and the Pt-catalyzed hydrogen-deuterium exchange of alumina hydroxyl groups (8). A priori, the migration of activated hydrogen may occur by surface diffusion or via the gaseous phase. This problem is treated in a recent paper by Vorontzov and Kochkina (9), who investigated the reduction of superficially oxidized plates of copper by interferometry. A platinum wire strongly promotes the reduction by H$_2$ when in direct contact with the plate and is even effective when separated from it.

At the present time, these questions have not been fully elucidated. Our contribution deals with the reduction of pure powdered nickel oxide. It emphasizes the fact that

chemical interactions of NiO with the impregnating reagents, such as chloroplatinic acid, are of great importance for the kinetics of reduction.

Methods and Results

NiO was prepared by thermal decomposition of Merck nickel nitrate at a final temperature of calcination of 950°C. The particles are of a rather homogeneous size (1μ). The specific area as determined by the BET method with argon was 1.1 m²/g. Traces of Na, Al, Al, Si, and Zr were detected by U.V. spectrography.

The kinetics of reduction were followed with a McBain thermobalance. The reactor and the conditions are described elsewhere (10). One-hundred mg powder was spread out on a layer of quartz fibers in a 15 mm diameter pan, and outgassed 15 hr at 200°C ($p = 3 \times 10^{-6}$ Torr). The reduction was carried out at 200°C ($p_{H_2} = 500$ Torr) and its degree expressed by α ($0 \leqslant \alpha \leqslant 1$). Generally, the evolved water was trapped at liquid nitrogen temperature. Some experiments, however, were made in the presence of water vapor ($p = 4.5$ Torr). In this case, the water vapor contacted the sample for 0.5 hr at 200°C before the introduction of hydrogen.

Benton and Emmett (11) have established that the reduction curves have a sigmoidal shape. Their quasilinear part has been used to define the apparent rate of reduction k_e (min⁻¹) by its slope, and the induction period t_i (min) by its intercept on the time axis, as shown in Fig. 3. For most solids, the reaction was nearly zero order in the 0.2–0.6 range.

I. Effect of Platinum

After impregnation of 5 g NiO with a calculated amount of H_2PtCl_6 solution, drying was carried out gently under shaking to obtain a homogeneous sample. Drying was completed at 110°C. Figure 1 shows the dependence of k_e on the temperature of precalcination in air. A pronounced maximum appears near 650°C. At lower temperatures some Cl⁻ ions remain on the solid and are strongly inhibi-
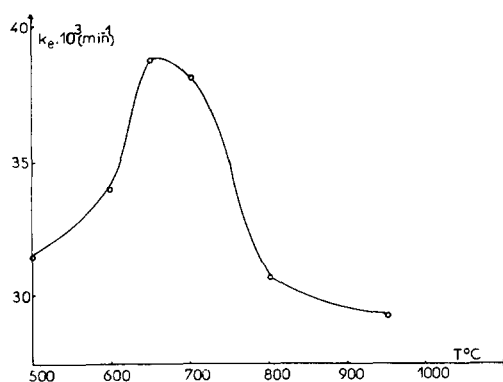

Fig. 1. Variation of k_e for NiO–Pt (0.215% Pt) when heated for 4 hr at various temperatures in air before reduction at 200°C.

tive for the reduction (12); at higher temperatures, Pt reorganizes and loses its promoting effect.

The variation of k_e with wt % Pt, after calcination in air at 650°C, is shown in Fig. 2. The rate of reduction increased from 11×10^{-3} min⁻¹ for the blank to 38×10^{-3} min⁻¹ at 0.15% Pt; above 0.15% Pt a plateau is observed. Extraction with hot water of two samples dried at 110°C (0.0538 and 0.538% Pt) removed 0.003 and 0.464 wt % Pt, 0.040 and 0.186 wt % Ni. Very few Cl⁻, if any, were fixed on the solids. The initial 0.538% Pt sample led, after extraction and drying at 110°C, to a k_e value of 31×10^{-3} min⁻¹. After heating in air at 650°C, k_e was 33×10^{-3} min⁻¹. Thus, most of the catalytic activity seems to be related to the fraction of Pt which is not extractable by water.
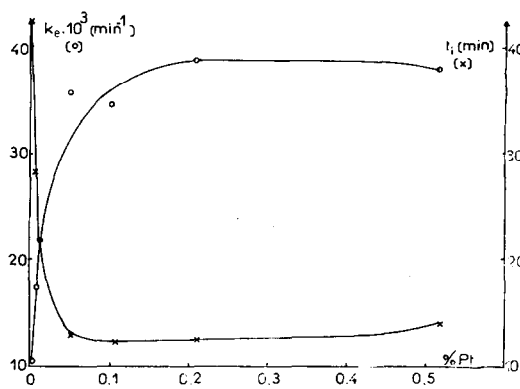

Fig. 2. Variation of k_e (o) and t_i (x) with % Pt.

In other experiments NiO was crushed during 24 hr before impregnation. $Pt(NH_3)_2(NO_2)_2$ was also used, and suspensions of NiO in both Pt reagents were submitted to ultrasonics for 2 hr. Total wt % Pt was 0.5. Residual percentage Pt and k_e values are collected in Table 1. Ultrasonics probably assist the strong chemisorption of water on NiO, as shown by the decrease of k_e from 11 to 3×10^{-3} min^{-1} in the absence of Pt. The main feature in Table 1 is that for a tenfold increase of percentage Pt (0.02 to 0.2), k_e is practically unchanged.

TABLE 1
FIXED WT % Pt AND RATE OF REDUCTION
IN DRY H$_2$

Impregnation with	Ultra-sonics	Residual % Pt	$k_e \times 10^3$ (min^{-1})
Water	No	0	11
Water	Yes	0	3
$Pt(NH_3)_2(NO_2)_2$	No	0.02	20
$Pt(NH_3)_2(NO_2)_2$	Yes	0.02	29
H_2PtCl_6	No	0.074	30.8
$\{H_2PtCl_6$ (Crushed NiO)	No	0.145	33.9
H_2PtCl_6	Yes	0.207	30.7

Moreover, if NiO impregnated with $Pt(NH_3)_2(NO_2)_2$ (0.512% Pt) and dried at 110°C was treated with H$_2$ at 100°C for reducing the platinum complex, the subsequent value of k_e was 33×10^{-3} min^{-1}. Also, no substantial increase of k_e was observed by mixing NiO with platinum or palladium blacks or with a Pt–Al$_2$O$_3$ catalyst (0.5% Pt) up to a wt % of 20.

When the reduction took place in wet hydrogen ($P_{H_2O} = 4.5$ Torr), the variation of k_e with percentage Pt (impregnation with H$_2$PtCl$_6$, calcination at 650°C) was similar to that in Fig. 2. However, the rate of reduction of the blank was much decreased (1.6 instead of 11×10^{-3} min^{-1}), while the value of k_e at the plateau was only slightly affected (34 instead of 38×10^{-3} min^{-1}).

II. Effect of Gold

HAuCl$_4$ was used for impregnation. At 0.26% Au, after calcination for 4 hr at 650°C, the rate of reduction in dry hydrogen was only 8.5×10^{-3} min^{-1}. But if the solid, only dried at 110°C, was extracted with water, $k_e = 26 \times 10^{-3}$ min^{-1}. For subsequent calcination at less than about 500°C, the rate of reduction remained approximately constant. On heating for 4 hr at 650°C, it fell from 26 to 15×10^{-3} min^{-1}. While 0.115% Ni was removed by water, 0.115 wt % Au was fixed on NiO.

III. Treatment with Other Salt Solutions

An amount of 0.5 wt % of the foreign cation was deposited on NiO. After heating to 110°C, as previously mentioned, and extraction with hot water, the residues were dried at 110°C and tested in reduction. The extracted solutions were tested for their nickel content and in a few cases for their foreign cation content. Table 2 shows the results, which are presented according to the periodic classification. Figure 3 shows the reduction curves for three particular solids. From chemical analysis, the Mg^{++} or Ca^{++} content was quite near zero, and the fixed amounts of Cu^{2+}, and Al^{3+} were respectively, 0.44 and 0.38%.

The H$^+$ and NH$_4^+$ cations were also tested. When NiO impregnated with HCl was simply dried, a very marked inhibition of the reduction occurred. If the impregnated solid was washed with pure water, the subsequent reduction curve had an irregular shape and it was not possible to
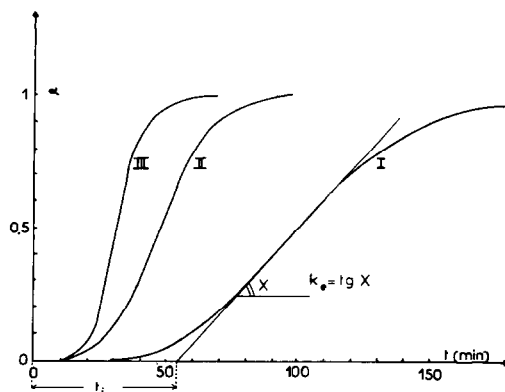

FIG. 3. Isotherms of reduction at 200°C in dry hydrogen of I, starting NiO; II, KCl treated NiO; and III, IrBr$_3$ treated NiO.

TABLE 2

EXTRACTED WT % Ni AND KINETIC DATA AFTER IMPREGNATION WITH DIFFERENT SALTS

Impregnation with		% Ni extracted	Reduction with dry H_2		Reduction with wet H_2	
Cation	Anion		$k_e \times 10^3$ min^{-1}	t_i min	$k_e \times 10^3$ min^{-1}	t_i min
No (pure water)	No	0.007	11	54	1.6	300
Li^+	Cl^-	0.003	10.7	43		
Na^+	Cl^-	0.006	25.3	34	11.0	125
K^+	Cl^-	0.008	27.3	30	12.6	126
Rb^+	Cl^-	0.003	24.9	52		
Cs^+	Cl^-	0.001	13.0	38	2.6	335
Cu^{2+}	NO_3^-	0.037	40.1	33	33.0	86
Ag^+	NO_3^-	0.028	18.7	40	9.0	184
Au^{3+}	Cl^-	0.115	26.1	28	10.4	172
Mg^{2+}	NO_3^-	0.008	23.6	35	11.6	115
Ca^{2+}	Cl^-	0.012	27.4	35	14.3	195
Sr^{2+}	Cl^-	0.005	25.0	33		
Ba^{2+}	Cl^-	0.004	25.2	46		
Zn^{2+}	SO_4^{2-}	0.03	8.5	45		
Cd^{2+}	SO_4^{2-}	0.009	11.0	61		
Hg^{2+}	NO_3^-	0.2	10.8	53	6.0	219
Al^{3+}	Cl^-	0.67	7.7	53		
La^{3+}	Cl^-	0.022	13.9	41	4.2	373
Fe^{3+}	NO_3^-	0.41	4.7			
Ru^{3+}	Cl^-	0.133	36.4	9.4		
Os^{3+}	Cl^-	0.085	53.4	12	37.3	23
Co^{2+}	NO_3^-	0.018	8.7	56		
Rh^{2+}	NO_3^-	0.117	45.0	13	33.3	25
Ir^{3+}	Br^-	0.07	53.9	21		
Ni^{2+}	Cl^-		23.1	41		
Pd^{2+}	Cl^-	0.073	33.5	31	19.1	95
Pt^{4+}	Cl^-	0.186	30.8	24	23.1	57

calculate k_e. Treatment with NH_4OH or NH_4Cl gave comparable results to that for NaCl.

In the case of K^+ the influence of the nature of the anion was examined. For Br^-, NO_3^-, SO_4^{2-}, ClO_3^-, ClO_4^-, k_e was about the same as in the Table 2. For PO_4H^{2-} it was lower (12.6×10^{-3} min^{-1}).

KCl and $OsCl_3$ treated samples were heated for 4 hr in air at different temperatures. With K^+, at 650°C, k_e fell to 17×10^{-3} min^{-1}. With osmium, 400°C was sufficient to restore the reactivity of the starting NiO.

DISCUSSION

Preferential development of reduction at the NiO–Ni interface has been postulated by Benton and Emmett (11). A priori, any modification of the solid or of the conditions of reduction, may affect the formation of nickel nuclei or (and) their growth. Therefore, it is necessary to develop methods which characterize both processes. In 1961, Delmon (13), considered the metallic nuclei as portions of spheres (Fig. 4a) and completed the theory of Mampel (14). By means of a detailed mathematical analysis of the reduction isotherms, the radial rate of growth of the nuclei k_i (cm min^{-1}) may be calculated. Elsewhere, we determine the intrinsic interfacial rate of reduction (k_I, min^{-1} cm^{-2} g) from adsorption measurements (15). k_I is correlated with k_i by $k_I = k_i \cdot \frac{\rho}{f}$, where ρ is the specific
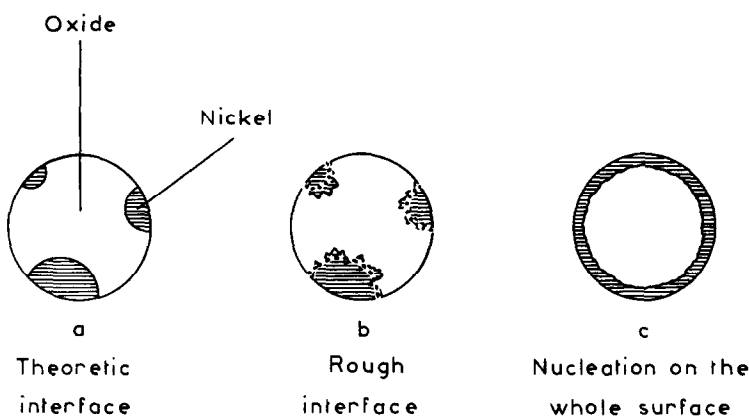
FIG. 4. Schematic representation of a partially reduced oxide particle.

gravity of NiO (6.3 g/cm^3) and f the roughness factor of the interfacial area (Fig. 4b). According to the model of Fig. 4b, k_i represents the linear rate of progression of the simplified interface (dotted line) and f the ratio of extents of real and simplified interfacial areas.

For the pure NiO used here (Sample B in paper 15a), $k_i = 1.2 \times 10^{-6}$ cm min^{-1}, $k_I = 2.6 \times 10^{-6}$ min^{-1} cm^{-2} g, $f \sim 3$, at 200°C. The rate of reduction which could be attained if the whole periphery of the solid was covered with metallic nuclei from the beginning of the reduction (Fig. 4c) may be estimated to be about 85×10^{-3} min^{-1}. It is much higher than the highest value observed in the presence of Pt (38×10^{-3} min^{-1}). Therefore, at the plateau of the curve $k_e = f(\%$ Pt) in Fig. 2, the reduction should take place with a Type 4b scheme. Accordingly, the outgassing of NiO–Pt (0.5%) at 350°C instead of 200°C leads, as for pure NiO (10, 16), to a substantial further increase of k_e (from 38 to 68×10^{-3} min^{-1}). Moreover, from microscopic observation of partially reduced NiO–Pt samples, the metallic nickel of which has been removed (10, 17), the reduction takes place from few superficial areas of the oxide.

One may ask why "free" platinum, formed from the water-extractible Pt reagent, is not able to accelerate very markedly the reduction. With respect to this question, the state of dispersion of Pt has been tested. X-Ray diffraction patterns and oxygen chemisorption measurements allow us to conclude that there is a poor dispersion of "free" Pt through the NiO powder, and obviously this may account for its low activity. But a slight increase of k_e with % Pt should be more expected than a plateau in Fig. 2. From this fact and the almost zero effect of platinum black at high content, we conclude that, if nickel nuclei are formed by migration of activated hydrogen, in our conditions this process only takes place up to quite short distances from the "free" Pt particles.

"Free" platinum in NiO–Pt (0.538%) treated at 650°C is partly alloyed with Ni, at about one Ni per Pt. Indeed, some particles with the corresponding structure are indicated by electron diffraction after ultrasonic dispersion of the powder in water. This alloy probably originates from precipitated NiPtCl$_6$ and apparently is not essential from a reduction kinetics point of view, since "free" Pt has about the same behavior when formed from either H$_2$PtCl$_6$ or Pt(NH$_3$)$_2$(NO$_2$)$_2$.

Analysis of extracted solutions of H$_2$PtCl$_6$, impregnated and dried solids, indicates exchange of some superficial Ni^{2+} by Pt^{4+} (2Ni^{2+}/1Pt^{4+}) and the dissolution of some NiO due to the acidity of the medium. There is satisfactory agreement between measured extracted percentage Ni^{2+} and the calculated one from total and extractable percent Pt.

Electron diffraction reveals an increase of crystalline parameter of NiO in presence of Pt (4.34 Å instead of 4.17 Å for pure NiO) at the edges of some particles. This deformation does not appear by reflexion examination of most of the surface. Therefore, the capture of Pt^{4+} at the surface of NiO is a rather localized process.

It is evident from Table 1 that $Pt(NH_3)_2(NO_2)_2$ reacts much less than H_2PtCl_6 with NiO, at given conditions of impregnation. This, joined to the very slight effect of "free" Pt, certainly accounts for the interesting observation by Nowak (4) about the much higher effectiveness of H_2PtCl_6 than $Pt(NH_3)_2(NO_2)_2$ for activation of his alumina supported nickel catalyst (0.6% Ni). The present results also explain why a nickel catalyst (20% NiO) is strongly promoted by Pt up to 0.1%, a higher Pt content being no more effective as mentioned in a patent (18).

We may ask what occurs when increasing the exchanged platinum content by varying the conditions of impregnation (Table 1). The modifications may have to do with the number of exchanging superficial areas or (and) their average Pt content. From the unchanged value of k_e when percentage Pt increases from 0.074 to 0.207, it may be assumed that the second parameter is preferentially affected.

The chemical analysis results indicate that $HAuCl_4$ gives rise to similar reactions as H_2PtCl_6, with a probable stoichiometry of the cationic exchange of two Au^{3+} per three Ni^{2+}.

The cations in Table 2 may be roughly divided into three groups according to the range of k_e values (Table 3). Ag^+ ($k_e = 18.7 \times 10^{-3}$ min^{-1}) particularizes itself by its position between Group I elements which have no favorable effect on the reduction and Group II elements for which k_e is 23 to 27×10^{-3} min^{-1}. First let us consider Group II. It contains Mg^{2+} and Ca^{2+}, the amount of which fixed by NiO is undetectable. Moreover, problematic Mg^{2+} or Cl^- traces should have a negative rather than positive effect on k_e. Indeed the very low reducibility of NiO-MgO solid solutions (19) and the inhibition by Cl^- are well established. As furthermore Group II includes elements of largely varying properties and the nature of anion is not very determining, the increase of k_e is not directly due to the fixation of small amounts of foreign elements by NiO. The assumption of a modification of the energy spectrum of the surface of the oxide is much more likely. Microcalorimetric measurements have allowed Gravelle, Marty and Teichner to prove that the reduction of pure NiO by CO starts from a limited number of superficial areas where the cation–anion bond is especially weak (20). The number and distribution of such areas may be modified by the treatments investigated here. Perhaps this occurs by migration of Ni^{2+} via the salt solution during the impregnation-drying process.

The difference of behavior of cations in Groups I and II (Table 3) is not completely elucidated. Certainly some salts used in Group I are able to precipitate some hydroxide by hydrolysis. They could then produce a blocking of part of the

TABLE 3

CLASSIFICATION OF CATIONS FROM KINETIC DATA

	Blank	Group I	Group II	Group III
Reduction with dry H_2	$k_e \times 10^3 = 11$	$k_e \times 10^3 \leqslant 11$–$13$	$k_e \times 10^3 \sim 23$–27	$30 < k_e \times 10^3$
Reduction with wet H_2	$k_e \times 10^3 = 1.6$	$k_e \times 10^3 \sim 2$	$k_e \times 10^3 \sim 12$	$20 < k_e \times 10^3$
Cations	Water	Li, Cs, Zn, Cd, Hg Al, La Fe, Co	Na, K, Rb, Mg, Ca, Sr, Ba Au Ni	Cu, Ru, Rh, Pd Os, Ir, Pt

surface for the reduction, because in all cases the corresponding compound is less reducible than NiO. This is experimentally proved for Al^{3+} at least, but does not hold for Li^+ and Cs^+ which strongly differ from Na^+, K^+, and Rb^+. The absence of interaction between Li^+, as lithia, and NiO near room temperature has already been pointed out (21).

Group III (Table 3) of the highest effectiveness includes metals of Group VIIIa of the periodic classification. The lack of Fe and Co in this group is ascribed to their low reducibility to the metal. Very likely, the modifications of the NiO surface which take place for Group II also occur for Group III. In this respect, H_2PtCl_6 for instance should have the same behavior as $HAuCl_4$. The foreign metal effect in Group III may be roughly evaluated by $(k_e - 0.025)$ min^{-1} where 25×10^{-3} min^{-1} is the mean reduction rate for Group II. The fixed amounts of Ru, Os, Rh, Ir, and Pd on NiO are not accurately known but, as the percentage Ni^{2+} extracted is largely higher than for Group II elements (except gold), it may be accepted that the order of magnitude is the same as for Pt or Au. Moreover, in the case of Pt, the exchanged cation content is not determining for k_e beyond a certain value. Figure 5 shows the variation of $(k_e - 0.025) \times 10^3$ with the percentage d character of the metallic bond (δ). Nickel excepted, the observed curve is quite comparable to that described by Sinfelt (22) for the specific catalytic activity in hydrogenolysis of ethane. Sinfelt explains the particular behavior of Ni in his experiments by the intervention of the geometric factor. The curve in Fig. 5 is also not fundamentally different from that found by Boudart and Ptak in the conversion of neopentane (23). Considering the number of elements involved, the similar variation of these very different parameters with δ cannot be altogether fortuitous.

The high promotive effect of copper is not surprising. Mixed NiO–CuO areas are highly reactive, with respect to the difference of reducibility of pure NiO and CuO,
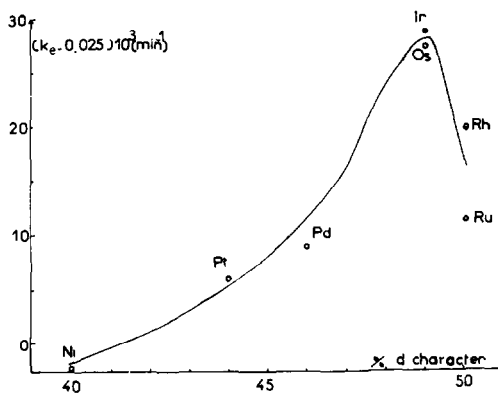

FIG. 5. Variation of $(k_e - 0.025) \times 10^3$ with percentage d character of the metallic bond in Ni, Pt, Pd, Os, Ir, Ru, and Rh.

and constitute preferential nucleation areas. Application of Mampel–Delmon theory to various NiO–Pt (up to 0.5% Pt) and to Ir or Os-treated NiO does not detect any substantial variation of k_i, the radial rate of growth of the nickel nuclei. Therefore, all the above observations must be ascribed to modifications of the single nuclei number. Natural nucleation areas are unique to the starting NiO. After treatment with salt solutions of Group II elements (Table 3), additional nucleation areas take part in the reduction and are similar to disorganized areas on the surface of NiO. For Group III, a last fraction of nickel nuclei should be formed from the exchanged foreign cations. Assume that the number of exchanging areas is in the same order of magnitude for Pt, Pd, etc. These various cations of high reducibility tend to be transformed into metal as soon as hydrogen contacts the sample at 200°C. During conversion to metal or once transformed into it, they should participate in the nucleation process with an effectiveness correlated to percentage d character of the metallic bond, presumably by activation of molecular H_2.

Another point of significant importance is the difference of thermal stability of the artificial nucleation areas according to the nature of the foreign cation. Pt is especially

favorable while osmium is very poor. The order of resistance to heat treatments (Pt, Au, Os) is the same as for the melting points T_M of PtO_2 (450°C), Au_2O_3 (160°C), OsO_4 (40°C) (24). The higher the T_M of the foreign oxide, the lower is the mobility of foreign cations at the surface of NiO and the more difficult is the reorganization of the surface NiO lattice.

The comparison of the rate of reduction in wet conditions with that observed in dry conditions shows a marked inhibition for pure NiO. Some indications, especially the very limited change of k_i, allow us to ascribe it to the blocking of some nucleation areas. For most Group II and III elements, $k_{e_{dry}} - k_{e_{wet}}$ is comparable to the rate of reduction of pure NiO in dry H_2. Therefore, the inhibition by water preferentially affects the natural nucleation areas and is of little effectiveness on the artificial ones. Generally speaking, a question arises then about how the "catalytic" effect of a foreign metal may be defined. Indeed, it is determined by the ratio of the observed rate of reduction to that of a blank. For instance, for NiO–Pt in Table 2 this ratio changes from less than three in dry conditions to 15 in wet conditions. But even if dry hydrogen is used, the reduction does not take place in a perfectly dry medium because of the water evolved. Therefore, divergent observations may be anticipated about the extent of the promoting effect of a given metal with rather moderate variations of the experimental procedure.

The discussion has been focused on the rates of reduction. The induction periods, t_i, are less reproducible than k_e. The average value of t_i is 36 min for Group II and 20 min for Group III elements (Table 3) while $t_i = 50$ min with the starting NiO. t_i and k_e have an opposite trend, as expected. No substantial further conclusion is drawn from t_i.

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