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Metal/Oxide Support Effects in the H_2–H_2O Deuterium Exchange Reaction Catalyzed by Nickel

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Catalysts of nickel supported on BeO, MgO, ZnO, Al_2O_3, Cr_2O_3, SiO_2, TiO_2, ZrO_2, ThO_2, and UO_2 have been prepared by coprecipitation with different precipitants and by impregnation of the basic nickel carbonate with a salt of the support. Nickel surface areas, which are required to measure the specific rates, were determined by hydrogen chemisorption. The fraction of nickel exposed increases when the support content is increased up to a saturation value. The most efficient supports for nickel dispersion are silica and alumina, while the least efficient is titania. Specific rates for hydrogen–water deuterium exchange over unsupported and supported nickel catalysts have been measured. Each support increases the specific catalytic activity value of nickel in comparison with that of the unsupported nickel. When the support content is increased, the specific catalytic activity increases up to a limiting value. This limit is attained when the number of metal–support contacts reaches a maximum. The most efficient supports are TiO_2 and ZrO_2, which increase the specific rate by about three orders of magnitude, and the least efficient are ZnO and SiO_2, which increase it only by one order of magnitude. The influence of the support on the specific catalytic activity is attributed to the participation of the support surface in the activation of the water molecule.

INTRODUCTION

The isotope exchange reaction of deuterium between hydrogen and water vapor

$$H_2 + HDO \rightleftarrows HD + H_2O \qquad (1)$$

is catalyzed by metals able to adsorb hydrogen in its atomic form, especially Group VIII metals, unsupported (*1–4*), supported (*5–11*), or metal alloys (*12*). Depending on the nature of the metal, the catalytic activity varies over a few orders of magnitude, the highest value being recorded for platinum (*1, 3–6, 8*) and the lowest for iron (*1, 6*).

As regards nickel catalysts for Reaction (1), Taylor (*13*) has evidenced a large increase of activity per gram of catalyst, r, by means of supporting the metal on various metallic oxides, nonreducible with hydrogen, like Cr_2O_3. Also Barb and others (*14, 15*) have shown that when adding to the metal nickel 4 at.% chromium (as chromia), r increases by about two orders of magnitude.

In previously published papers, we have shown that chromia (*16*) and alumina (*17*) can influence the r value for Reaction (1) in two ways, namely increasing the nickel metallic surface area per gram of nickel, S'_{Ni}, via preventing metal sintering during nickel oxide reduction with hydrogen, and, at the same time, increasing the catalytic activity per nickel surface area unit, r_s, the so-called specific rate or specific catalytic activity. Both effects have shown a saturation trend versus support oxide percentage. While alumina preserves a higher dispersion of nickel than chromia is able to do, the latter is more efficient in enhancement of the specific rate of reaction.

Sagert and others (*18*) have also shown

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TABLE 1

Average Values of the Metallic Crystallite Size, d_{Ni}, Obtained from Hydrogen Chemisorption, X-Ray Diffraction, and Electron Microscopy

Catalyst	Composition No. of M atoms	Metallic crystallite size, d_{Ni}, Å		
	Total No. of (Ni + M) atoms (%)	H_2 Chem.	XRD	EM
Ni/Cr_2O_3	30	190	—	160
Ni/SiO_2	20	74	94	80
	40	80	90	—
Ni/MgO	20	151	160	165
	40	84	96	—
Ni/Al_2O_3	15	77	80	84
	15	98	95	90
	40	75	70	67

that the value of r_s for Reaction (1) for catalysts composed of 80 mol% nickel/20 mol% oxide support is strongly influenced by the nature of the oxide support. The supports were again Cr_2O_3, as well as MoO_2, WO_3, MnO, or UO_2. The authors attempted to explain the experimental data as being due to changes of the Fermi level in the metal induced by an electron transfer between metal and support. However, in the presence of the support, the actual change in the electron concentration in the metal is negligibly small (*19*, *20*), at least within the range of the metallic crystallite sizes ($d_{Ni} >$ 100 Å) reported in the paper (*18*).

In the present paper an attempt is made to determine how the nickel dispersion and the catalytic activity could be influenced by support nature.

EXPERIMENTAL

1. Catalyst Preparation

The following two methods were used.

(a) Water-soluble salts, preferably nitrates, were coprecipitated with Na_2CO_3, NaOH, $(NH_4)_2CO_3$, or oxalic acid. After filtration the precipitate was washed with twice-distilled water, dried at 105°C, calcined in flowing nitrogen at 340°C, and reduced in flowing hydrogen at 350°C. The detailed procedure has been described previously (*16*). Reduction completeness has been checked by TG analysis.

(b) Basic nickel carbonate was impregnated with various nitrates dissolved in water. After drying and calcining, the oxide mixture has been processed as described previously (*16*).

Since in Ref. (*13*) it has been shown that alkali ions act as a poison on the nickel catalytic activity for Reaction (1), we have thoroughly removed the alkali from the precipitate by washing it with twice-distilled water. At the same time, reactants which do not introduce alkali ions in the course of preparation were used.

2. Total Surface Area Measurement

The BET surface areas of the samples have been measured using krypton adsorption at liquid nitrogen temperature. A surface area of 19.5 $Å^2$ per krypton atom has been used (*21*).

3. Metallic Nickel Dispersion Measurements

Three independent methods have been developed.

(a) Hydrogen chemisorption at room temperature. It was assumed that: (i) the amount of hydrogen chemisorbed at 100 Torr constitutes a monolayer (*22*); (ii) one hydrogen atom is chemisorbed on each surface metallic nickel atom; and (iii) each nickel atom occupies 6.5 $Å^2$ (*23*).

Under the same conditions, hydrogen adsorption on support samples was negligible and it was considered to be negligible in the presence of nickel, too.

(b) Transmission electron microscopy of the very thin specimens cut with an ultramicrotome from catalyst samples embedded in Araldite (*24*). The metal crystallite sizes lie around the average values, given in Table 1, within about a standard deviation of 11 Å.

(c) X-Ray diffraction line broadening, using Co*K* radiation filtered through iron.

In Table I average values of metallic crystallite sizes calculated from hydrogen chemisorption ($d_{Ni} = 5/\rho\ S'_{Ni}$, ρ = specific weight of nickel) are compared with the values obtained from X-ray diffraction, as well as from electron micrographs. Since the values obtained via these independent methods are reasonably consistent, only hydrogen chemisorption has been used systematically throughout the study.

4. *Kinetic Measurements*

The catalytic activity of each sample was measured in a dynamic reactor (*25*), as described previously (*16*). The hydrogen flow, containing about 50 ppm deuterium, was bubbled through water containing about 4 at.% deuterium, then passed through the catalyst bed. Saturation temperature was 63.5°C and catalyst temperature was 79°C, except where specified otherwise.

Undesired effects of capillary condensation (*26*) and back diffusion (*25*) were prevented. To avoid possible effects of inner diffusion, samples with various grain size of one of the most active catalysts have been studied. From the results obtained it could be concluded that up to 0.25-mm grain size, the effect of inner diffusion can be neglected. For less active catalysts this size limit is even higher. Therefore, grain sizes of less than 0.25 mm have been used throughout the study for measuring the catalytic activity.

RESULTS AND DISCUSSION

Various samples of supported nickel catalysts have been prepared using one or both preparation methods described above. The hydrogen chemisorption area, S_{Ni}, as well as the catalytic activity, r, both per gram of catalyst, have been measured. Hence, the value of the specific catalytic activity, r_s, was calculated. Also, taking into account the nickel content in the sample, the value of the metallic surface area per gram of nickel, S'_{Ni}, was calculated. The following supports were used: BeO, MgO, ZnO, Al_2O_3, Cr_2O_3, SiO_2, TiO_2, ZrO_2, ThO_2, and UO_2. It should be emphasized that the nickel oxide and any support, as well as any support–nickel oxide mixture, have no catalytic activity under given conditions as described above.

1. *Influence of Support Nature on Nickel Dispersion*

Figures 1a and b show the nickel surface area per gram of nickel, S'_{Ni}, versus support content, expressed as percentage of the total number of metal atoms. The trend reported previously for Ni/Cr_2O_3 (*16*) and Ni/Al_2O_3 (*17*) is also observed for other samples of supported nickel: the fraction of nickel exposed increases when the support content is increased, up to a saturation value. The support content at which the saturation value S'_{Ni} is attained depends on the nature of the support: this is reached at rather low values of the content for some supports (about 10 mol% for Ni/ThO_2, Ni/Al_2O_3, Ni/UO_2, and Ni/BeO), while for others it is attained at higher content (about 20–30 mol% for Ni/SiO_2, Ni/MgO, and Ni/TiO_2). It should be emphasized that the saturation value of S'_{Ni} for Ni/Cr_2O_3 samples does not change with the preparation method used. For Ni/MgO the saturation value is influenced by the precipitant used: the fraction of nickel exposed is higher for the samples prepared by coprecipitating with oxalic acid than for those obtained by coprecipitating with sodium hydroxide. On the other hand, there are catalysts which exhibit a clear trend for further increase of nickel dispersion, even if the support content was increased up to 40 mol% Zr (for Ni/ZrO_2), or even 80 mol% Zn (for Ni/ZnO). In this latter case, the nickel dispersion is influenced by the precipitant nature, too.

The average saturation values S'_{Ni} (at high support content) reported in Figs. 1a and b can be arranged in an increasing order, as is summarized in Table 2. In fact, a higher value of S'_{Ni} means a more efficient way to prevent nickel crystallite growth during the reduction with hydrogen at 350°C. Therefore, a possible relationship between the

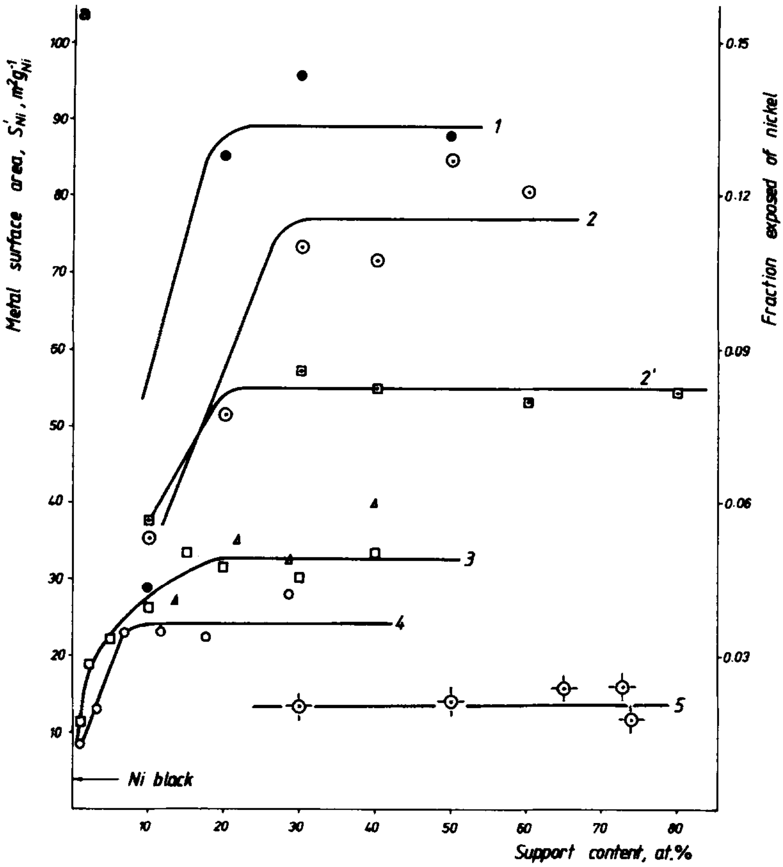

FIG. 1. Effect of different supports on nickel dispersion, with preparation routes indicated. (1) ●—Ni/SiO_2, obtained by coprecipitating nickel nitrate with mixture of sodium silicate and sodium carbonate; (2) ⊙—Ni/MgO, coprecipitating nickel and magnesium nitrate mixture with oxalic acid; (2') ⊡—Ni/MgO, coprecipitating nickel and magnesium nitrate mixture with sodium hydroxide; (3) □—Ni/Cr_2O_3, coprecipitating nickel and chromium nitrate mixture with sodium carbonate (partially published in Ref. (*16*)); Δ—impregnating basic nickel carbonate with chromium nitrate; (4) O—Ni/ThO_2 impregnating basic nickel carbonate with thorium nitrate; (5) ⌖—Ni/TiO_2, coprecipitating nickel nitrate and titanium tetrachloride mixture with sodium carbonate; (6) ◬—Ni/Al_2O_3, coprecipitating nickel and aluminum nitrate mixture with sodium carbonate (partially published in Ref. (*17*)); (7) ⊕—Ni/ZrO_2, coprecipitating nickel nitrate and zirconium oxychloride with sodium carbonate; (8) ∇—Ni/UO_2, impregnating basic nickel carbonate with uranyl nitrate; (9) + Ni/BeO, impregnating basic nickel carbonate with beryllium nitrate; (10) ×—Ni/ZnO, coprecipitating nickel and zinc nitrate mixture with oxalic acid; (10') + Ni/ZnO, coprecipitating nickel and zinc nitrate mixture with sodium carbonate.

relative fraction of nickel exposed reported in Table 2 and the support particle size is expected. To assess the average particle size of the support in the nickel catalyst samples, the value of the BET area of the same samples have been used. In previous papers (*16, 17*) it has been shown that on plotting the difference between S_{BET} and S_{Ni} versus chromia or alumina weight percentage, a straight line was obtained in each case. Hence the chromia or alumina surface area per gram of support (S_s) is practically independent of the sample composition. For the other eight series of supported nickel catalysts, when representing the values of the difference $S_{BET} - S_{Ni}$ versus

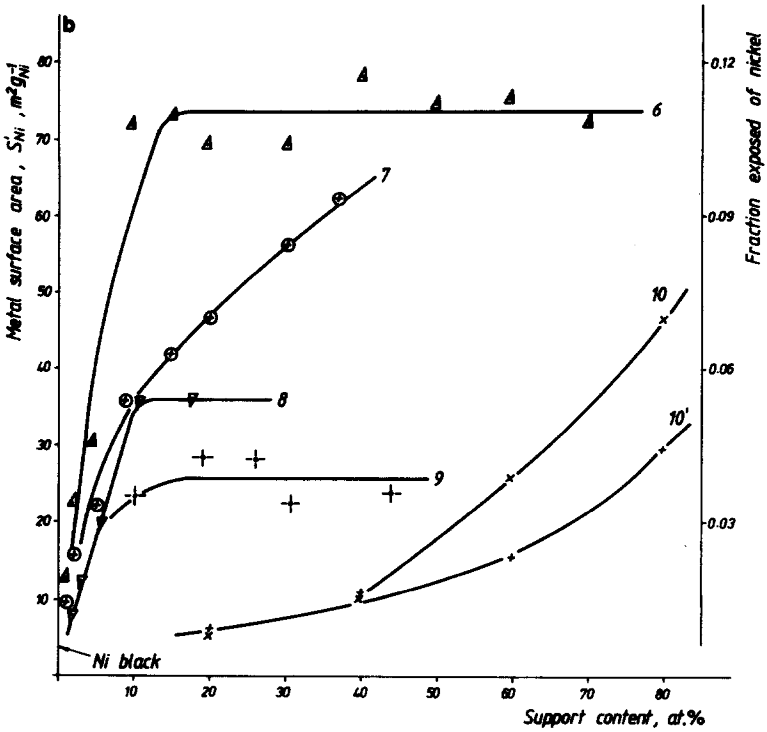

FIG. 1—*Continued.*

weight percentage of support, an approximately straight line was obtained and the values S_s of average surface area per gram of support was calculated. The average support particle size, d_s, could be derived as $d_s = 5\ \rho_s^{-1}\ S_s^{-1}$, where ρ_s is the specific weight (density) of the support. The d_s values are also quoted in Table 2. It can be seen that, in fact, no such simple relationship could be established between the value of the relative fraction of nickel exposed and the support average particle size, d_s. In addition, other factors, such as interaction between the metal and the support, seem to become involved in preventing nickel crystallite growth. Thus, the stability of the small metallic crystallites is improved by partial wetting of the support by metal particles (*27*). Unfortunately, in the literature there are few data for the adhesion energy between metallic nickel and support oxides (*20, 28*). For example, the adhesion energy for nickel on alumina is 0.645 J m^{-2} and for nickel on beryllium oxide is 0.187 J m^{-2}. From our data (Table 2) it can be seen that alumina does actually prevent metallic nickel crystallite growth more efficiently than beryllium oxide.

TABLE 2

Average Values of the Nickel Surface Area for Nickel Catalyst with High Support Content

Catalyst[a]	S'_{Ni} (m^2/g_{Ni})	Relative fraction of nickel exposed	Support average particle size, d_s (Å)
Ni black	4.4	1	—
Ni/TiO_2	14	3.2	82
Ni/ThO_2	24	5.5	68
Ni/BeO	26	5.9	132
Ni/Cr_2O_3	32	7.3	17
Ni/UO_2	36	8.2	123
Ni/ZrO_2	55[b]	≥12.5	86
Ni/MgO	55[c]	12.5	42
	77[d]	17.5	53
Ni/Al_2O_3	74	16.8	26
Ni/SiO_2	89	20.2	26

[a] Ni/ZnO is not included.

[b] S'_{Ni} saturation value may have not been reached.

[c] NaOH as precipitant.

[d] Oxalic acid as precipitant.

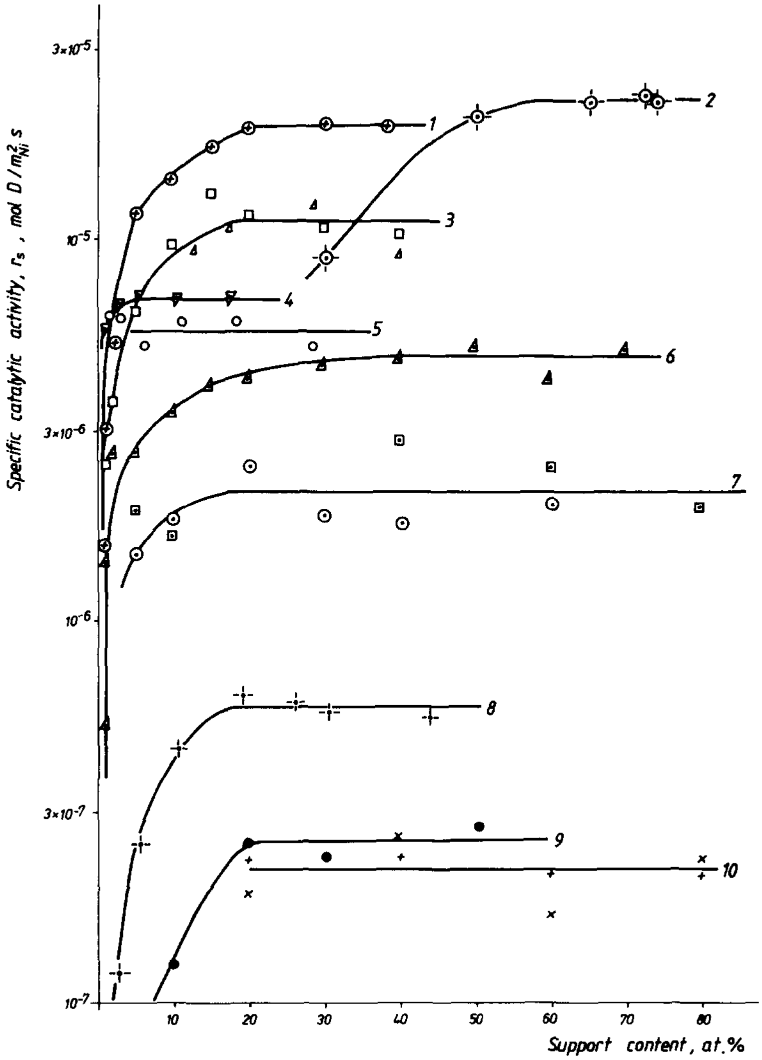

FIG. 2. Effect of different supports on specific catalytic activity. The samples are those given in Figs. 1a and b. (1) ⊕—Ni/ZrO_2, (2) ⊙ —Ni/TiO_2, (3) □—Ni/Cr_2O_3, coprecipitating (partially published in Ref. (*16*)), or △—impregnating; (4) ▽—Ni/UO_2; (5) ○—Ni/ThO_2; (6) ▲—Ni/Al_2O_3 (partially published in Ref. (*17*)); (7) ⊡—Ni/MgO, coprecipitating with sodium hydroxide, or ⊙—coprecipitating with oxalic acid; (8) +—Ni/BeO; (9) ●—Ni/SiO_2; (10) ×—Ni/ZnO, coprecipitating with oxalic acid, or +—coprecipitating with sodium carbonate. Specific catalytic activity for unsupported nickel is 1.7 × 10^{-8} mol D/m^2_{Ni}s.

2. *Effect of the Nature of the Support on the Specific Catalytic Activity*

The specific activities of the nickel catalysts on different supports are plotted in Fig. 2 versus the support content. As the support content of the sample increases, the r_s value increases up to a limit depending on the support. The behavior is similar to that described previously for Ni/Cr_2O_3 and Ni/Al_2O_3 catalysts. The nature of the support plays an essential role in determining the saturation value of the specific catalytic activity. However, the latter is not in-

TABLE 3

Average Values of Specific Catalytic Activity for Nickel Catalysts with High Support Content

Catalyst	Specific activity in moles of deuterium per sec per m² of nickel ($r_s \times 10^6$)	Relative specific activity	d_{Ni} (Å)
Ni black	0.017	1	1280
Ni/ZnO	0.22	13	—[a]
Ni/SiO_2	0.26	16	63
Ni/BeO	0.60	35	216
Ni/MgO	2.2	129	102[b] 73[c]
Ni/Al_2O_3	4.7	276	76
Ni/ThO_2	5.7	335	234
Ni/UO_2	6.9	406	156
Ni/Cr_2O_3	11.0	665	176
Ni/ZrO_2	19.7	1160	102[d]
Ni/TiO_2	22.6	1330	401

[a] For Ni/ZnO catalysts there is no saturation value of S'_{Ni}.

[b] Coprecipitated with sodium hydroxide.

[c] Coprecipitated with oxalic acid.

[d] The d_{Ni} value may be too high.

fluenced by the preparation method or by the nature of the precipitant used.

The r_s average saturation values from Fig. 2 can be arranged in the increasing series given in Table 3. As can be seen, the specific activity, in comparison with that of the unsupported nickel, is enhanced about three orders of magnitude in the case of the titanium dioxide and zirconium dioxide, while zinc oxide and silicon dioxide enhanced it only about one order of magnitude. Other supports lie between these extreme cases.

The influence of the nature of the support on the specific catalytic activity of metals has constituted a rather controversial issue in the literature. Although a majority of the data published, concerning a broad variety of reactions, show that the support role is limited to that of increasing the metal dispersion, papers describing results for the ethane hydrogenolysis on supported nickel (*29*), carbon oxide–hydrogen synthesis reactions on supported nickel (*30*), ethene hydrogenation on supported platinum (*31*), and water–toluene dealkylation on supported rhodium (*32*) have provided evidence that the r_s value of the metal used depends on the support nature. The opinion of Boudart (*33*) should be mentioned: the answer whether specific catalytic activity will be influenced by the support nature would be positive for demanding reactions and negative for facile reactions.

In order to check whether this is the case for the catalyst samples used in this paper, kinetic measurements of benzene hydrogenation (known as a facile reaction) have been carried out on MgO-, Al_2O_3-, Cr_2O_3-, and SiO_2-supported nickel, as well as on unsupported nickel. The reaction temperature was 70°C and the saturation temperature 6°C. The specific catalytic activity lies between 7×10^{-8} (for Ni/SiO_2) and 13×10^{-8} (for Ni/Cr_2O_3) moles C_6H_6 hydrogenated per second per square meter of nickel. Thus the r_s values for benzene hydrogenation on nickel catalysts vary by not more than a factor of two, whereas, from Table 3 it can be seen that r_s values for the H/D exchange reaction between hydrogen and water vapor on the same catalysts range up to more than two orders of magnitude.

The reason for such a strong support effect for Reaction (1) is not readily apparent. It cannot be correlated either with average nickel crystallite size, as shown in Table 3, or with the average support particle size reported in Table 2. Also, it cannot be correlated with the presence in the catalyst of some combination between nickel oxide and support; indeed, the sample of nickel on alumina in which the spinel $NiAl_2O_4$ is present shows about the same value of specific catalytic activity as does the sample without spinel. From Table 3 it can be seen that the nickel crystallite sizes are large enough that the influence of electron transfer between metal and support on the r_s values should be excluded, too (*19, 20*).

An interesting correlation can be established by plotting the r_s values of the nickel catalysts versus the ratio of the support

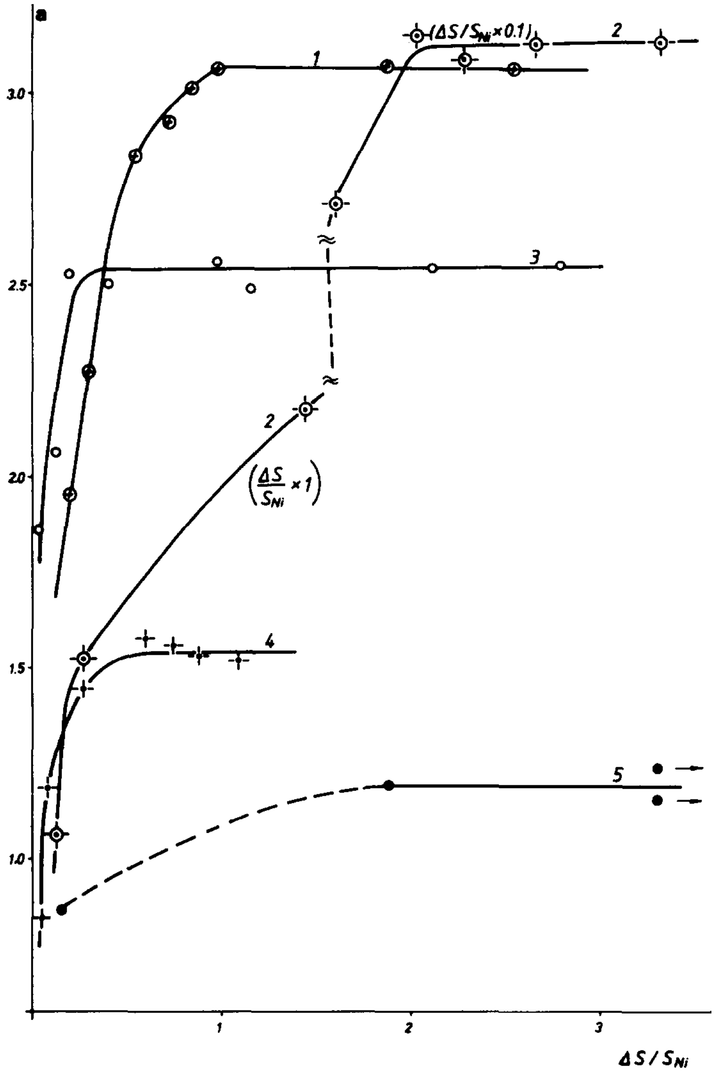

FIG. 3. Relative specific catalytic activities versus the ratio of support to metallic surface areas. The samples are those given in Figs. 1a and b. (1) ⊕—Ni/ZrO_2; (2) -⌖- —Ni/TiO_2; (3) ○—Ni/ThO_2; (4) + —Ni/BeO; (5) ●—Ni/SiO_2; (6) ▽—Ni/UO_2; (7) □—Ni/Cr_2O_3; (8) △—Ni/Al_2O_3; (9) ⊡—Ni/MgO, coprecipitating with sodium hydroxide, or ⊙—coprecipitating with oxalic acid; (10) ×—Ni/ZnO, coprecipitating with oxalic acid, or +—coprecipitating with sodium carbonate.

area, ΔS ($\Delta S = S_{BET} - S_{Ni}$), to the metallic surface area, S_{Ni}. Both areas are expressed in square meters per gram of sample. For convenience, in Figs. 3a and b are represented log r_s/r_s^0, where r_s^0 is the specific catalytic activity of the unsupported nickel.

Again, a trend to an upper limit of r_s values can be seen, but on this plot the limit is reached when the value of the support surface area is comparable with the value of the metallic surface area. This can be interpreted as an optimal composition associated with obtaining the highest possible number of contacts between nickel and support particles. This fact bears the supposition that metal–support contacts are catalytically more active than the metal surface alone. When the content of the support is

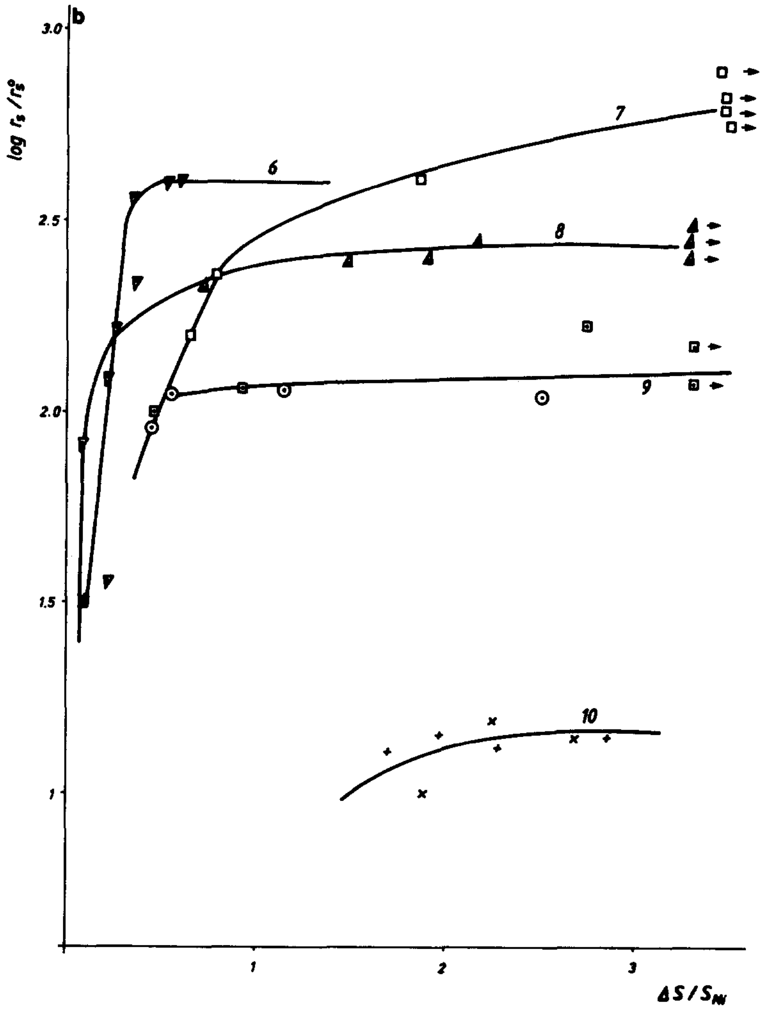

FIG. 3—*Continued.*

lower than the optimal one, the number of metal–support contacts is small and the r_s value is lower than the r_s limit value. When the support content exceeds the optimal one, it will not result in an additional number of contacts, and therefore r_s remains at the limiting value characteristic of each support.

The number of nickel–support contacts may be considered in connection with the work of adhesion between the two kinds of solid particles. When the nickel–support interaction is quite strong, the maximum number of contacts is attained for a $\Delta S/S_{Ni}$ ratio up to unity. From Figs. 3a and b it can be seen that this is the case for the majority of the supported nickel catalysts. On the contrary, when the interaction between support and metal is weak, the maximum number of nickel–support contacts will be attained for a $\Delta S/S_{Ni}$ ratio much higher than unity. The support particles tend to agglomerate in three-dimensional islands, and therefore a large excess of support is necessary to provide the maximum number of nickel–support contacts. This is the case for the Cr_2O_3- and TiO_2-supported nickel catalysts, when the maximum contact number is attained for the ratio $\Delta S/S_{Ni}$ of 2.5 and 20, respectively.

The enhancement of the nickel specific activity is due to intimate contacts between the metal and the support which arise during the preparation process of the catalyst. The mechanical mixtures obtained by crushing together alumina or chromia with nickel powder show the specific catalytic activity value of the unsupported nickel catalyst. Therefore simple nickel–support contacts formed during the mixing by crushing have no effect on the r_s value.

3. *Mechanism of Reaction*

Rolston and Goodale (*10*), who have studied Reaction (1) on Pt/Al_2O_3 as catalyst, proposed that it takes place between chemisorbed hydrogen on the platinum surface and adsorbed water on the support surface. Supposing that, in their working conditions, the metal surface is completely covered with adsorbed hydrogen and that water adsorption on the support surface follows a Langmuir isotherm, the authors derived a simple law rate expression of the form

$$\frac{P_{H_2}}{r} = k' + k'' P_{H_2O}. \qquad (2)$$

On the other hand, Temkin and co-workers (*34, 35*) considered that Reaction (1) occurring on the metal surface follows a two-step mechanism (an oxidation followed by a reduction):

$$\mathrm{HDO} + (\ \ ) \rightleftarrows \mathrm{HD} + (\mathrm{O}) \qquad (3)$$

$$\mathrm{H_2} + (\mathrm{O}) \rightleftarrows \mathrm{H_2O} + (\ \ ) \qquad (4)$$

where ( ) is the vacant site on the metal surface, and (O) is the site occupied by chemisorbed oxygen. The authors supposed that the metal surface is energetically heterogeneous, the adsorption energy of the water varying linearly with the coverage. In this case the water adsorption is described by a Temkin isotherm

$$\Theta = \frac{1}{a} \ln c_0 P_{H_2O}, \qquad (5)$$

where a and c_0 are constants. The authors derived a rate law expression of the type

$$r(1 + b) = kb^m, \qquad (6)$$

where $b = P_{H_2}/P_{H_2O}$, and m is a constant whose value ranges between 0 and 1.

Aiming to check the reaction mechanism, kinetic measurements have been performed on the nickel catalysts presented in this paper by varying the water vapor pressure, P_{H_2O}. The results can be plotted either as $P_{H_2}\, r^{-1}$ versus P_{H_2O}, or as $\log r(1 + b)$ versus $\log b$. In both cases, the experimental data showed linear dependences for all catalysts studied; therefore, kinetic data are not conclusive to support one or the other of the mechanisms suggested.

However, from literature data concerning hydrogen and water adsorption on unsupported nickel, it would appear that the two-step mechanism is less probable. Thus Zakumbaeva and co-workers (*36*), studying by microcalorimetry the chemisorption of hydrogen and water on the surface of nickel black, found that the metallic surface covered with chemisorbed hydrogen cannot chemisorb water vapor.

Having in mind that the passivated nickel catalyst samples should be first activated via heat treating them "*in situ*" with hydrogen (*16*), it follows that the metallic surface of the activated nickel catalyst samples is saturated with chemisorbed hydrogen. Therefore, on this surface, also, the first step [Reaction (3)] in the two-step mechanism of Reaction (1) is impossible.

The results presented in this paper on the influence of the support on the specific catalytic activity of the nickel for Reaction (1) can be interpreted by a mechanism in which the activation of both reactants is necessary. The surface of metallic nickel activates the hydrogen molecule by dissociative chemisorption. However, this surface covered with hydrogen cannot chemisorb water, or does so to an insignificant extent. This fact can explain the very low value of the specific catalytic activity of the unsupported nickel.

The water molecule can be activated on the surface of those metal oxide supports which can interact easily and reversibly with water. If the metal nickel is deposited on such supports, forming tight metal–support contacts, then the metal–support boundaries allow a faster reaction between water activated on the support surface and hydrogen, activated on the metal surface. In this way would be explained the influence of the support and, also, of the number of the metal–support contacts on the specific catalytic activity of the nickel for Reaction (1).

In the literature hydrocarbon reforming reactions with water vapor are cited in which the support effect on the specific catalytic activity of the metal is also explained by the participation of the support in the activation of the water molecule (*32, 37, 38*). In this case it is supposed that the activated species of the water are the surface hydroxyl groups which migrate on the support surface towards the metal–support frontier, where they react with the hydrocarbon molecules activated on the metal surface.

As regards Reaction (1), it is difficult to suppose that the migration of the support hydroxyl groups can play any role, because the reaction is fast at temperatures much lower than those used in the catalytic hydrocarbon reforming reactions with water vapor. Therefore, one may assume that on the support surface the water molecule would be activated by hydrogen bonds and migrates as such toward the metal–support contact where the exchange reaction occurs. The rate of the process which takes place on the support surface has to depend on the chemical nature of the support. In this way, the specific catalytic activity of the nickel for Reaction (1) also depends on the support nature.

Thus, water activation by the support appears to be a necessary condition to increase the specific catalytic activity of nickel. This is not sufficient; the support–nickel contact as obtained during catalyst preparation should be a tight one, otherwise the activated water molecules cannot meet activated hydrogen. The latter case occurs when the support is mechanically mixed with nickel powder; then the specific catalytic activity equals that of the unsupported nickel.

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