JOURNAL OF CATALYSIS 42, 350–359 (1976)

Surface Properties of Hydrogen-Reduced Nickel Chrysotiles

C. L. KIBBY, F. E. MASSOTH,[1] AND H. E. SWIFT

Gulf Research and Development Company, P. O. Drawer 2038, Pittsburgh, Pennsylvania 15230

Received December 9, 1975

Hydrogen reduction of tubular nickel and nickel magnesium chrysotiles in a microbalance produced high Ni surface areas (10–30 m^2/g) and uniform size distributions centered about 3 nm at 250°C and increasing to a mean of 8 nm at 550°C. The areas, measured by O_2 chemisorption, were higher at the higher temperatures due to more complete reduction, which was difficult in a single step, especially with Mg present. High temperature reduction and reoxidation, followed by a second reduction at 350–450°C, raised the Ni areas to 35–50 m^2/g. Reduction of a high area, flake-type nickel chrysotile gave much lower Ni areas (2–7 m^2/g) and mean Ni crystallite diameters greater than 20 nm.

INTRODUCTION

As part of our investigation of synthetic layered silicates and aluminosilicates, a study of nickel and magnesium chrysotiles was undertaken to evaluate the reduction of nickel and to determine subsequent nickel areas by oxygen chemisorption. Noll and co-workers (*1*, *2*) have reported the synthesis, surface areas, and structural properties of chrysotile $Mg_3(OH)_4Si_2O_5$, garnierite $Ni_3(OH)_4Si_2O_5$ (nickel chrysotile), and $Co_3(OH)_4Si_2O_5$. Stable BET surface areas of 110, 125, and 165–190 m^2/g were reported for these respective compounds. Recently, pore size distributions for chrysotile and garnierite were reported as calculated from electron microscopy (*3*). In that study excellent electron micrographs of synthetic chrysotile and garnierite are given. In the case of chrysotile the hollow-needle shape of the crystallites is very evident. Synthetic garnierite also forms as needle-shaped crystallites, although there are unusual crystal growth and growth defects. It was determined that the mean internal radius of the hollow rods was 3.7 nm and the mean external radius was 12.9 nm which compare to respective values reported by Noll of 3.7 and 12.0 nm.

A recent series of patents report the synthesis of high surface area chrysotiles and their catalytic applications (*4*). These high surface area chrysotiles have flakelike morphology with surface areas ranging from 250 to 500 m^2/g.

For purposes of comparison, studies on the reduction of nickel in a high surface area flake-form of nickel chrysotile and in a mixed $NiO\text{-}SiO_2$ material are included in this investigation.

EXPERIMENTAL

Nickel chrysotile (sample I) and nickel magnesium chrysotile (sample II) having surface areas of 110 and 103 m^2/g, respectively, were prepared at the Baroid Division of NL Industries. These materials

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[1] Present address: Department of Mining, Metallurgical, and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112.

were synthesized according to the procedure used by Noll and co-workers (*1*, *2*). Sample I contained 44.6% nickel, which is slightly less than the formula $Ni_3(OH)_4Si_2O_5$ would predict. Sample II had a nominal composition of $Ni_{2.75}Mg_{0.25}(OH)_4Si_2O_5$ but was analyzed to contain 42.1% nickel, which, like sample I, is slightly lower than expected. In both cases about 0.2 SiO_2 has to be added to the formula to give the analyzed nickel content. Samples I and II exhibited similar X-ray diffraction patterns which agreed with patterns reported by Noll and co-workers (*1*, *2*). Sample III was prepared at Gulf Research according to the method reported by Robson to obtain a high surface area flake-form of chrysotile (*4*). This material had a BET area of 266 m^2/g. Sample IV consisted of a mixture of nickel and silicon oxides with a nominal composition of $3NiO \cdot 2SiO_2$. This sample was also prepared at Gulf Research by dissolving 227 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 75 ml of water and thoroughly mixing this solution with 180 g of Ludox AS silica (DuPont Corp.) in a blender. The resultant material was dried at 120°C for 16 hr, followed by calcination at 500°C for 10 hr.

Reduction–oxidation (redox) cycles were carried out with 100-mg catalyst samples in a flow microbalance (*5*) at atmospheric pressure using alternately 100 cm^3/min of H_2 and air. Purges in N_2 were made between charges of reactive gases. Catalyst pretreatment prior to the redox cycles consisted of heating the sample at temperature overnight in air. Oxygen was removed from N_2 when desired by switching an Oxy Trap (Alltech Associates) into the flow line.

DATA TREATMENT

Most of the research reported in this paper centered around the reduction of nickel chrysotile in hydrogen. The amount of nickel reduced could not be determined simply from the measured weight loss during reduction, even though water retention was not significant, because either one or two molecules of water could be formed for each nickel atom:

$$Ni^{2+} + H_2 = Ni^0 + 2H^+ \quad (1)$$

$$2H^+ + 2OH^- = 2H_2O \quad (2)$$

$$2H^+ + O^{2-} = H_2O. \quad (3)$$

Dehydroxylation of structural OH groups also occurred without hydrogen:

$$2OH^- = O^{2-} + H_2O. \quad (4)$$

The latter reaction can be considered a combination of reactions (2) and (3), however.

Fortunately, it was found that reduced samples could be reoxidized in air with essentially no further dehydroxylation, so that the weight change during reoxidation could be identified with the reaction:

$$Ni^0 + \tfrac{1}{2}O_2 = NiO. \quad (5)$$

The complete dehydroxylation and reduction of a sample, plus reoxidation, allowed an estimate of the dry weight and, from that, the amount of water adsorbed on the surface before high temperature treatment.

The surface areas of the nickel in reduced samples were determined by purging with oxygen-free nitrogen, cooling to below 100°C, then changing slowly from nitrogen to air flow. Nickel areas were measured by oxygen chemisorption according to (*6*):

$$Ni^0\ (\text{surface}) + O_2 = Ni(O_2). \quad (6)$$

The reoxidation was then completed by heating in air to the desired temperature. Diffusion of oxygen into nickel takes place at room temperature (*6*), but, under the conditions used in the microbalance, that uptake was slow and could be distinguished from chemisorption at the surface. Figure 1 shows the weight changes in a typical reduction–chemisorption–reoxidation experiment.

Defining ΔW_R, ΔW_C, and ΔW_O as weight changes in reduction, O_2 chemisorption, and reoxidation, respectively (absolute

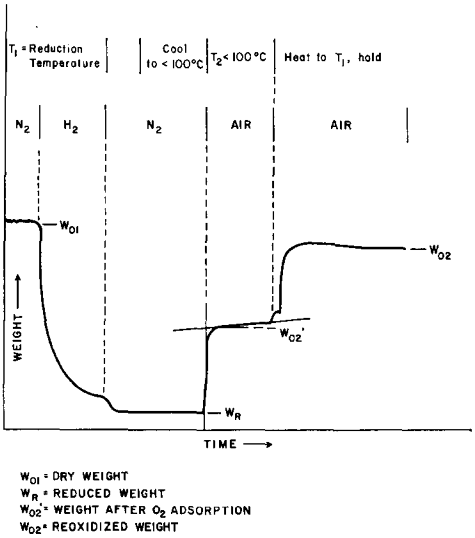

FIG. 1. Typical reduction–reoxidation experiment. Nickel chrysotile reductions and surface areas.

values in milligrams), then:

$$\Delta \mathrm{Ni}^0 = \Delta W_{\mathrm{O}}/16, \tag{7}$$

$$\Delta(\mathrm{OH}) = (\Delta W_{\mathrm{R}} - \Delta W_{\mathrm{O}})/9, \tag{8}$$

$$\Delta \mathrm{Ni}^0 \text{ (surface)} = \Delta W_{\mathrm{C}}/32, \tag{9}$$

where ΔNi^0, $\Delta(OH)$, and ΔNi^0 (surface) are the amounts of reduced nickel, lost hydroxyl groups, and surface nickel (in millimoles).

TABLE I

Surface Areas and Pore Volumes of Nickel Chrysotiles

Sample	Pore volume (cm^3/g)	Average pore radius (nm)	BET area (m^2/g)
Sample I ($Ni_3(OH)_4Si_2O_5$)			
As received	0.35	6.5	110
Calcined, 400°C	0.34	6.5	106
Calcined, 500°C	0.37	6.6	114
Sample II ($N_{2.75}Mg_{0.25}(OH)_4Si_2O_5$)			
As received	0.30	5.9	103
Calcined, 400°C	0.33	6.3	104
Calcined, 500°C	0.34	6.3	108

Nickel surface areas were calculated using a value of 0.065 nm^2 per surface nickel atom (*7*), and an average nickel crystallite diameter was calculated as:

$$\bar{d} = \frac{6V}{A}$$

$$= \frac{6(0.0109 \text{ nm}^3/\text{atom})\Delta \mathrm{Ni}^0}{(0.065 \text{ nm}^2/\text{atom})\Delta \mathrm{Ni}^0 \text{ (surface)}}, \tag{10}$$

$$\bar{d} = 2\Delta W_{\mathrm{O}}/\Delta W_{\mathrm{C}}, \text{ nm}. \tag{11}$$

The average diameter calculated is a minimum value, for regular polyhedra or spheres; crystals with specific area/volume ratios greater than 6 would have larger diameters.

The number of crystallites was estimated crudely, for cubic crystals, as

$$n = \frac{\text{total volume Ni}^0}{\text{average volume/crystal}}$$

$$= \left(\frac{\text{weight Ni}^0\text{, mg}}{\text{density, mg/nm}^3}\right) \div (\bar{d}\text{, nm})^3. \tag{12}$$

For spheres, n would be twice as large, and n is also dependent on the particle size distribution.

RESULTS

Properties of Ni- and NiMg-Chrysotile Samples Investigated

Most of the research was done using samples I and II which were described in the experimental section. Table 1 gives surface area, pore volume, and average pore radii values obtained from these samples. The surface area obtained for the nickel chrysotile sample is very close to the value reported by Noll and co-workers (*1*, *2*). Incorporation of magnesium in the nickel chrysotile resulted in little change in the surface and pore properties. The X-ray diffraction patterns of these samples were essentially the same as reported by Noll and co-workers. Heating nickel chrysotile in air resulted in partial dehydroxylation as low as 350–400°C. At 450°C complete collapse of the structure occurred; however, little change in the surface area and pore properties resulted. Incorporation of some magnesium in nickel chrysotile (sample II) raised the temperature needed to collapse the structure by about 50°C. It was interesting to note with samples I and II that, even though complete collapse of the structure occurred by heating at high temperatures, no distinguishable lines could be observed by X-ray diffraction, not even NiO.

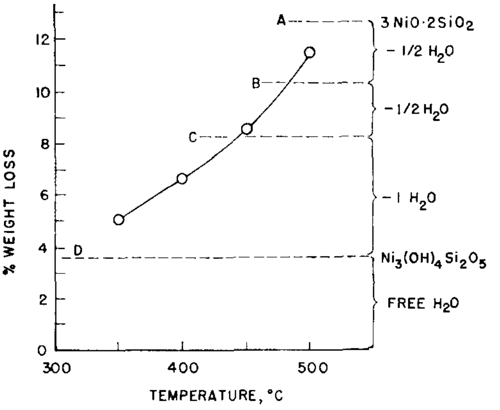

FIG. 2. Weight loss on heating Ni-chrysotile in air.

Figure 2 shows the weight loss on heating nickel chrysotile in air. At 350°C some dehydroxylation occurred and at 450°C the equivalent of one-half of the OH's were removed (line C). Line B represents the weight loss when only the internal OH's remain, i.e., one OH per unit cell. At 500°C these are partially removed with complete dehydroxylation (line A), leaving only NiO and SiO_2.

Chemical analysis of sample I (dry) gave 44.6% nickel, which is slightly less than the formula $Ni_3(OH)_4Si_2O_5$ would predict, even allowing for adsorbed water. Assuming that the extra material is silica, then an additional 0.24 SiO_2 is needed, as shown by the values in Table 2. The adsorbed water is 3.6%, structural water 8.8%, and reducible oxygen 11.7% by weight. Reducible oxygen is defined as that left after complete dehydration, i.e., one oxygen per nickel. Sample II had a nominal composition of $Ni_{2.75}Mg_{0.25}(OH)_4Si_2O_5$. Chemical analysis of this sample for nickel

TABLE 2

Nickel Chrysotile Formulas

Formula	Molecular weight	Dry weight	Wet weight	H_2O weight	Oxygen weight
Sample I					
3 Ni	176.13	44.61	43.00		
O	16.00	4.05	3.91	—	3.91 O
4 OH	68.03	17.23	16.61	8.79 H_2O	7.82 O
2 SiO_2	120.17	30.43	29.34		11.73% O
0.24 SiO_2	14.50	3.67	3.54		
0.84 H_2O	14.75	100.00%	3.60	3.60 H_2O	
	409.58		100.00%	12.39% H_2O	
Sample II					
2.75 Ni	161.45	42.07	40.85		
0.25 Mg	6.08	1.59	1.54		
O	16.00	4.17	4.05	—	3.04 O
40 H	68.03	17.72	17.21	9.12 H_2O	8.09 O
2 SiO_2	120.17	31.31	30.40		11.13% O
0.2 SiO_2	12.03	3.14	3.05		
0.64 H_2O	11.46	100.00%	2.90	2.90 H_2O	
	395.22		100.00%	12.03% H_2O	

TABLE 3

Reduction of Sample I (Nickel Chrysotile)[a]

Pretreat in air	Weight (mg)	Reduction in H_2	Weight changes		
			R[b] (mg)	O2[c] (mg)	OX[d] (mg)
500°C, 2 hr	90.85	500°C, 65 hr	−13.5	+2.55	10.5
500°C, 2 hr	88.6	350°C, 16 hr	−10.0	+3.40	11.3
500°C, 2 hr	89.9	400°C, 16 hr	−10.55	+4.15	12.05
500°C, 2 hr	91.5	450°C, 16 hr	−12.25	+4.15	12.05
500°C, 2 hr	91.3	350°C, 16 hr	−12.05	+4.15	12.0
500°C, 2 hr	91.25	260°C, 65 hr	−10.5	+3.85	(10.5)

Reduction (%)	Ni area		Ni crystal size (av, nm)	
	(m^2/g)	(m^2/g Ni)		
86	30	70	8.1	500°C
93	40	93	6.6	350°C
99	49	113	5.8	400°C
99	49	113	5.8	450°C
99	49	113	5.8	350°C
86	45	105	5.1	260°C

[a] Dry weight = 100.4 mg. Runs on one sample, in order shown. Nickel analysis gave 44.6% Ni by weight on dry weight basis.

[b] R = reduction.

[c] O2 = oxygen chemisorption.

[d] OX = oxidation, 12.2 = 100%.

was also slightly lower than expected, i.e., 42.1%. About 0.2 SiO_2 added to this formula gives the proper nickel content as shown by the data in Table 2. In addition to 2.9% adsorbed water, there is 9.1% structural water which can be lost by dehydroxylation and 11.1% reducible oxygen (MgO is assumed to be inert). For both samples, the adsorbed water amounted to 1 water molecule/nm^2, or about one monolayer.

Hydrogen Reduction of Ni and NiMg-Chrysotile Samples

In Table 3, data are shown for a series of reductions and oxidations at 260–500°C for sample I. These data were obtained from one sample, run in the order shown. Essentially complete nickel reduction was accomplished resulting in a maximum nickel area of 50 m^2/g and a crystallite size of 5.8 nm. This was constant for reductions at 350, 400, and 450°C and appears to be limited by the chrysotile structure. All that is necessary to maximize nickel area is complete reduction at a temperature low enough so that sintering isn't severe. The redox treatment at high temperatures (reoxidation was at 500°C in each case) accomplished this and actually decreased the average crystal size in these experiments. Electron microscopy revealed a narrow distribution of nickel crystallites formed by reduction in hydrogen.

The initial experiments on the NiMg-chrysotile sample (II) were designed to measure the extent of reduction of this sample at various temperatures and to test the oxygen chemisorption technique. To obtain accurate nickel metal contents, a redox cycle was run without the low temperature oxygen chemisorption. Then a second reduction was run for only 1 hr, and the oxygen chemisorption tried. The data

TABLE 4

Reduction of Sample II (NiMg-Chrysotile)

Pretreat in air	Reduction #1 in H_2	% R	Reoxidation in air	Reduction #2 in H_2	% R	Ni area		Ni crystal size (av, nm)
						(m^2/g)	$(m^2/g$ Ni)	
350°C, 16 hr	350°C, 1 hr	11.1	350°C, 1 hr	350°C, 1 hr	13.7	6.6	16.5	5.8
350°C, 16 hr	350°C, 2 hr	14.4	350°C, 1 hr	350°C, 1 hr	14.8	8.3	20.7	5.0
350°C, 16 hr	350°C, 3 hr	16.1	350°C, 1 hr	350°C, 1 hr	15.7	9.1	22.9	4.8
400°C, 16 hr	400°C, 7 hr	35.1	400°C, 16 hr	400°C, 1 hr	32.6	13.2	33.1	6.9
400°C, 16 hr	400°C, 7 hr	37.0	450°C, 16 hr	350°C, 1 hr	15.2	8.5	21.3	5.0
450°C, 16 hr	450°C, 7 hr	57.0	450°C, 16 hr	450°C, 1 hr	49.1	16.0	40.0	8.6
450°C, 16 hr	450°C, 7 hr	53.8	450°C, 16 hr	350°C, 1 hr	21.5	9.6	24.1	6.3

obtained are given in Table 4. After 7 hr at 450°C, only half of the nickel was reduced. Reductions at higher temperatures were more complete but resulted in larger crystal sizes. However, these were reduced to about 5 nm for reductions at 350°C after a prior high temperature redox treatment.

In a second set of experiments on one sample, redox and oxygen chemisorption were done at successively higher temperatures. As shown in Table 5, the extent of reduction was only 84% after severe treatment at 500 and 550°C. In this series, the average crystallite size steadily grew from 4.9 to 8.7 nm, but the area increased since more nickel reduced each time and the highest area obtained was 27 m^2/g. In Fig. 3A, the surface areas are shown as a function of reduction temperature. Also shown are data from Table 4 for separate runs and a calculated curve for the areas obtainable if the crystal size did not in-

TABLE 5

Reduction of Sample II (NiMg-Chrysotile)

Pretreat in air	Reduction in H_2	% R	Ni crystals		
			Area		Size (av, nm)
			(m^2/g)	$(m^2/g$ Ni)	
16 hr, 350°C	350°C, 5 hr	18.7	10.7	27.4	4.9
16 hr, 400°C	400°C, 5 hr	35.6	20.1	51.6	4.9
16 hr, 450°C	450°C, 5 hr	56.6	24.4	62.5	6.5
16 hr, 500°C	500°C, 5 hr	65.0	26.1	66.8	7.1
16 hr, 550°C	550°C, 5 hr	77.2	25.8	66.2	8.4
1 hr, 500°C	500°C, 65 hr	84.3	27.0	69.2	8.7

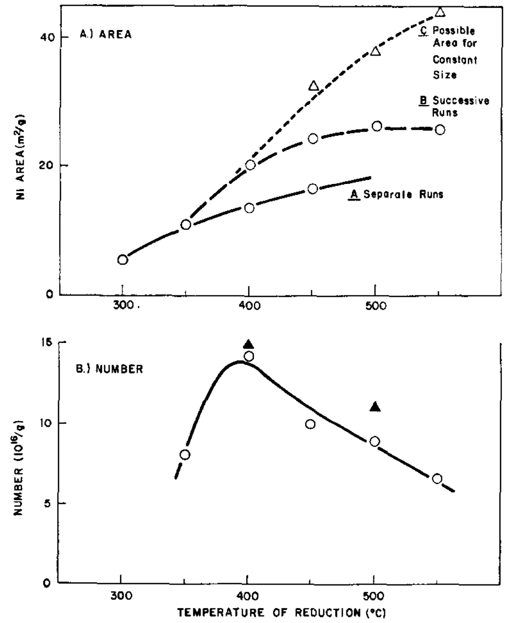

FIG. 3. Number and area of nickel crystals. NiMg-chrysotile reduction.

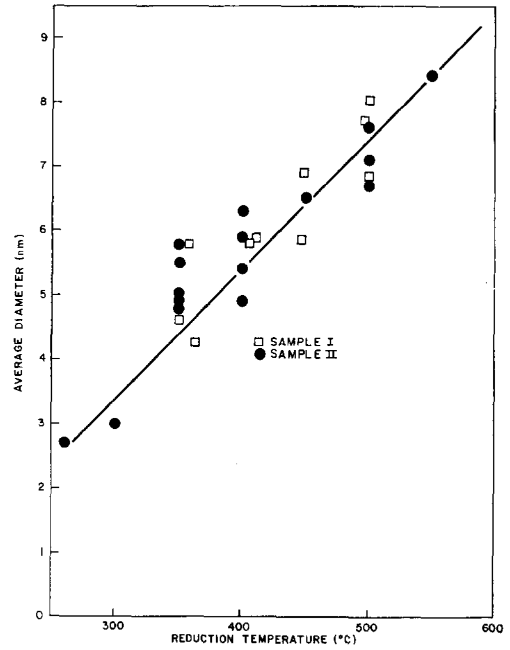

FIG. 4. Crystallite size vs reduction temperature. NiMg-chrysotile, sample II, and Ni-chrysotile, sample I.

crease with temperature. In Fig. 4 the change in crystal size with temperature is shown and, in Fig. 3B, the number of crystallites (assuming all are of average diameter). The latter can be compared to the estimated number of crystallites in the original chrysotile, as shown in Table 6. It is seen that they are quite close. A possibility for the uniform crystal sizes and lack of sintering observed in nickel chrysotile reduction is that one nickel crystallite is formed from each chrysotile crystal.

In Table 7, data are shown for low temperature reductions of nickel magnesium chrysotile without any previous calcination. Very small crystallites were formed in this way, but the extents of reduction were so small that the total areas were not very large. At the other extreme, a sample calcined at 600°C, then reduced at 350°C, yielded crystal sizes of about the same magnitude but reduced more extensively so gave a higher nickel area.

In Table 8, data for a series of runs designed to test the redox treatment for development of nickel surface area are summarized. The catalyst was alternately reduced at 500 and 400°C, with intervening 500°C calcinations. In each case, following a 500°C redox with a 400°C reduction lowered the crystal size by about 1 nm, lowered the extent of reduction by 10%,

TABLE 6

Reduction of Sample II (NiMg-Chrysotile)

Reduction temperature (°C)	Ni crystal size (av, nm)	Number of Ni crystallites (cubic)[a] ($\times 10^{16}$ g^{-1})
350	4.9	7.8
400	4.9	14.3
450	6.5	10.0
500	7.1	8.9
550	8.4	6.5

[a] Number of support crystals (same basis) = 5×10^{16} g^{-1}; using 3.3 g/cm^3 density, 100 m^2/g area, 225 cm^3/mole. Diameter of support crystals (av) = 18 nm.

TABLE 7

Reduction of Sample II (NiMg-Chrysotile)

Pretreat	Reduction in H_2	% R	Ni crystals		
			Area		Size (av, nm)
			(m^2/g)	(m^2/g Ni)	
None	2 hr, 260°C	1.8	1.9	4.9	2.7
Air, 260°C, 1 hr	16 hr, 300°C	5.5	5.1	13.0	3.0
Air, 300°C, 1 hr	2 hr, 350°C	10.1	5.1	13.0	5.5
Air, 350°C, 1 hr	16 hr, 350°C	21.0	10.8	27.8	5.4
Air, 600°C, 1 hr	16 hr, 350°C	32.4	16.7	42.7	5.4

and increased the area. The area increased with time, regardless of the reduction temperature.

In Fig. 4, data for the crystallite sizes are shown for samples I and II. It can be seen that they are almost identical under the same conditions. Apparently, magnesium has little effect on crystal growth in hydrogen. It does stabilize the chrysotile structure to reduction or thermal degradation. In Fig. 5, the weight changes during a standard calcination and reduction are quite different for these samples.

Hydrogen Reduction of High Surface Area Nickel Chrysotile and a Nickel Oxide–Silica Mixture

Sample III (high surface area nickel chrysotile) was difficult to reduce, and the nickel sintered. The data in Table 9 show that the average nickel crystallite sizes were greater than 20 nm for reductions conducted between 350 and 500°C.

Sample IV (mixed oxides of nickel and silicon) was reduced at 400°C, after calcination at 500°C. A weight loss corresponding to 84% reduction of $3NiO \cdot 2SiO_2$ was

TABLE 8

Reduction of Sample II (NiMg-Chrysotile)

Pretreat in air	Reduction in H_2	Weight changes[a] (mg)			
		% R	R	O2	OX
500°C, 16 hr	500°C, 5 hr	63	−7.5	+1.9	+7.2
500°C, 16 hr	400°C, 5 hr	57	−6.4	+2.1	+6.6
500°C, 16 hr	500°C, 5 hr	70	−8.0	+2.4	+8.0
500°C, 16 hr	400°C, 5 hr	64	−7.4	+2.5	+7.4

Dry weight, +97.5 mg

Ni area		Ni crystals	
(m^2/g)	(m^2/g Ni)	(av, nm) Size	($\times 10^{15}$) Number
23.7	58.0	7.6	6.8
26.2	64.2	6.3	10.9
30.0	73.5	6.7	11.1
31.2	76.2	5.9	14.7

[a] R = reduction.

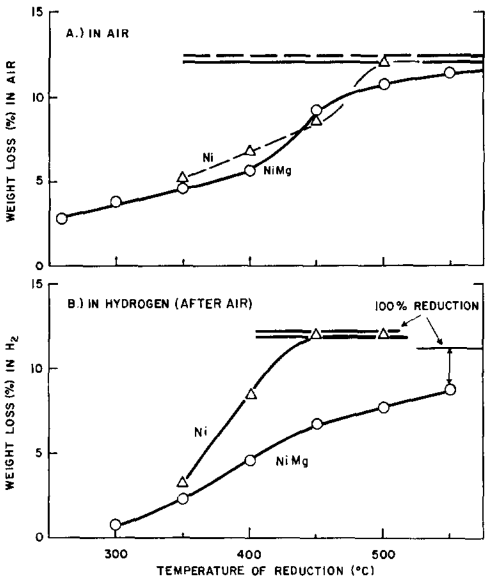

Fig. 5. Comparison of Ni-and NiMg (Ni/Mg = 11)-chrysotiles at high temperatures.

observed. The nickel surface area was only 8.6 m^2/g, and the average crystallite size 33.3 nm. Since the reduction was for only 1 hr, it is obvious that the NiO in this mixture reduces easily and the nickel formed sinters readily. This was not unexpected and demonstrated that the microbalance conditions were not too mild and that the oxygen chemisorption method does give lower areas when expected.

DISCUSSION

The oxygen chemisorption method detects small changes in relative nickel surface areas reproducibly and is rapid and convenient. When followed by complete oxidation to determine the total amount of reduced metal, it provides an estimate of the average crystallite size. The assumption that two oxygen atoms are adsorbed for each surface nickel atom (*6*) was checked by comparing the crystal diameters so calculated with minimum diameters estimated from electron microscope measurements (Table 10). The agreement is fairly good, and much better than that for the assumption of one oxygen per surface nickel atom (*8*). The latter assumption would double the nickel surface areas to values (70–100 m^2/g) which seem rather high. At this time, however, it is not clear that the value of two oxygens per surface nickel atom is correct.

TABLE 9

Reduction of sample III High Area Ni-Chrysotile

Pretreatment in air	Weight (mg)	Reduction in H_2	Weight changes[a] (mg)		
			R	02	OX
350°C, 16 hr	99.0	350°C, 5 hr	−4.65	+0.225	+2.45
400°C, 16 hr	96.55	400°C, 5 hr	−5.3	+0.3	+3.90
450°C, 16 hr	94.6	450°C, 5 hr	−5.75	+0.4	+5.15
500°C, 16 hr	92.95	500°C, 5 hr	−8.25	+0.5	(+7.0)

Reduction (%)	Ni area		av, Ni crystal size (nm)	Temp
	(m^2/g)	(m^2/g Ni)		
22	2.75	6.9	21.8	350°C
35	3.7	9.2	26.0	400°C
46	4.9	12.2	25.7	450°C
63	6.1	6.1	28.0	500°C

[a] As in Table 3.

The rationale for incorporating magnesium into nickel chrysotile was twofold. First, as a nonreducible ion, magnesium should help stabilize the structure under reducing conditions. Second, by occupying lattice positions, it should restrict movement of nickel, thus inhibiting sintering.

It was found that the magnesium forms were indeed more stable towards reduction. However, the sintering of nickel crystallites in hydrogen was not serious with the magnesium-free chrysotiles.

Only in thermal, and especially hydrothermal stability, might the magnesium forms prove superior. It is apparent that there is something special about tubular chrysotile which allows the growth of uniformly small nickel crystals, even after the structure is degraded by thermal treatment in air.

Reducing the nickel chrysotile at high temperatures gives moderately high nickel surface areas. The reduction of samples I and II in hydrogen produced crystallites of average diameter 4–8 nm and nickel surface areas of 20–30 m²/g. Contrary to expectations, high temperature redox treatments actually lowered the crystallite sizes obtained on subsequent reductions at low temperature, and increased the nickel areas to 35–50 m²/g. Apparently, the NiO formed initially during reoxidation breaks into fragments, and the fragments may be reduced at milder conditions without sintering. Extended reoxidation was not as effective in reducing crystallite sizes; the NiO fragments must sinter slowly at 500–550°C.

No greater resistance to nickel metal sintering was found with nickel magnesium chrysotile in pure hydrogen. Both nickel and nickel magnesium chrysotile gave stable, high nickel surface areas, although the latter reduced less than the pure nickel sample. There was no evidence that any significant amount of nickel was reincorporated into a nickel silicate structure during reoxidation; reduction rates upon subsequent reduction at low temperature were always much greater than for previously unreduced samples.

A high area nickel chrysotile and a nickel oxide silica catalyst both sintered badly in hydrogen, giving low nickel areas and large (20–30 nm) crystallites of nickel, under the same conditions which produced high nickel areas with tubular nickel chrysotile.

TABLE 10

Comparison of Oxygen Adsorption and Electron Microscope Values for Nickel Crystal Sizes

Sample[a]	Minimum mean diameters (nm)	
	Oxygen uptake	Electron microscope
I	6	8
I	5	8
II	9	10
III	28	40
IV	33	100

[a] As defined in text, I and II are tubular chrysotiles, III is a flake-type chrysotile, IV is NiO on silica.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to the Baroid Division of NL Industries for preparing some of the nickel chrysotile samples; also, to Mr. Robert Halter for conducting the microbalance measurements and to Mr. Paul Ahner for the electron microscope data.

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