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The Use of a Niobia–Silica Surface Phase Oxide in Studying and Varying Metal–Support Interactions in Supported Nickel Catalysts

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A surface phase oxide, containing niobia (Nb_2O_5) deposited onto silica (SiO_2), was prepared as a catalyst support for nickel. The niobia concentration was varied to give an equivalent surface coverage of one to three monolayers. Physical characterization techniques including X-ray diffraction (XRD) and analytical transmission microscopy indicated that the niobia overlayer distributed quite uniformly over the silica substrate during preparation. When these samples were heated at 873 K for 2 h or longer, the deposited niobia phase in the two- and three-monolayer supports sintered into niobia crystallites as detected by XRD, but the one-monolayer support remained stable. As a catalyst support for nickel, this one-monolayer system exhibited chemical behavior characteristic of strong metal–support interaction as shown by hydrogen chemisorption, ethane hydrogenolysis, and carbon monoxide hydrogenation. Under comparable conditions, the extent of interaction is weaker for the niobia–silica surface phase oxide than for bulk niobia. In the limit of the most severe reduction treatment used, this difference in support behavior is attributed to the inability of the surface phase oxide for compound formation.

INTRODUCTION

The work of Tauster and co-workers (*1, 2*), which identified several binary oxides as interacting supports, has in subsequent years led to a large number of studied on the unique adsorption and catalytic behavior exhibited by many transition metals supported on these oxides (*3*). Recently, evidence has been mounting for the presence of an oxide species on the metal surface as the cause for the unusual chemical properties. Specifically, this has been suggested for titania-supported iron (*4*), rhodium (*5–7*), nickel (*8–10*), and platinum (*7, 11, 12*) from studies on supported-metal catalysts and model systems alike. These studies have significantly enhanced our understanding on the mechanism of the so-called strong metal–support interaction (SMSI). Perhaps the one point which still remains unclear is whether the interaction is solely a site-blocking effect or involves an electronic component.

At any rate, there is now little doubt that the SMSI effects are real. It would thus be desirable to be able to systematically vary the extent of interaction. We recently attempted to achieve such a goal with niobia-supported nickel catalysts (*13*) by establishing a reliable gauge on the interaction and identifying the pertinent parameters which affect it. These parameters include the reducibility of the support, the metal crystallite size, and the severity of reduction treatment. We also showed that niobia behaves similarly to titania as an interacting support and proposed the same mechanism of interaction for both oxides.

One other parameter which holds promise for manipulating metal–support interaction is the concentration of the interacting support. An interacting oxide can be incorporated into another oxide to form a binary system in basically one of two ways. The first way is to deposit it as a *surface phase oxide* onto the other oxide, as done by Murrell and Yates for titania–silica (*14*). In a surface phase oxide, an oxide substrate is coated with another oxide in the form of a

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thin layer. The second way is to precipitate both oxides as a *mixed oxide*, as done by Wang *et al.* for titania–alumina (*15*). In this case the two oxides are likely to be present homogeneously in the bulk phase. Both methods of preparation result in supports which exhibit the characteristic SMSI behavior (suppression in hydrogen chemisorption) for rhodium (*14*) and platinum (*15*) catalysts. Although these studies established the feasibility of using combinations of oxides in studying metal–support interactions, there has been relatively little attention paid to this approach. In particular, there are few examples in the literature which report on the activity and selectivity of catalysts supported on oxides containing an interacting component and an inert one.

In this paper the results of our recent work with a nickel catalyst supported on a niobia–silica surface phase oxide will be presented. The preparation and physical characterization of the support will first be described, followed by a discussion of the chemical properties of the catalyst in hydrogen chemisorption, ethane hydrogenolysis, and carbon monoxide hydrogenation. These data will be compared with those for silica- and niobia-supported nickel catalysts, and interpreted with respect to the current understanding of SMSI.

EXPERIMENTAL

Preparation. The niobia–silica (Nb_2O_5–SiO_2) support was prepared by impregnating silica (SiO_2, Davison Grade 952) with a hexane solution of niobium(V) ethoxide (Alfa Products) to incipient wetness. This step was conducted in a glovebox filled with argon to minimize any reaction of the precursor with moisture in the air. The impregnated sample was placed in a vacuum oven and dried overnight to remove the solvent. It was then decomposed in flowing nitrogen (18 liters/h) at 673 K for 2 h and calcined in flowing oxygen (18 liters/h) at 773 K for 2 h. As shown below, this treatment produced a relatively homogeneous monolayer of Nb_2O_5 on SiO_2. The procedure could be repeated to deposit a second and a third monolayer of Nb_2O_5. The amount of niobium(V) ethoxide required in each step was obtained from a stoichiometric calculation based on the experimentally determined BET surface area of the substrate. In this calculation each $NbO_{2.5}$ unit mesh in the niobia layer was assumed to occupy a surface area of 16 $Å^2$. This assumption will be discussed later.

A nickel catalyst was prepared with the Nb_2O_5–SiO_2 support by the incipient wetness impregnation of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Fisher Scientific). The metal loading is 9% by weight, as confirmed by atomic absorption measurements. The impregnated sample was dried in air at 373 K overnight, then stored before use.

Physical characterization. BET surface areas of the supports were measured with a commercial Quantasorb unit (Quantachrome Corp.). Transmission electron microscopy (TEM) studies were performed in a JEOL JEM 120CX instrument equipped with a PGT System IV Analyzer for energy dispersive analysis. TEM samples were prepared by placing a drop of a suspension of finely meshed particles in toluene on a carbon-covered copper grid.

Powder diffraction patterns of supports and catalysts were obtained with a Rigaku D/Max diffractometer using Mo radiation. The average nickel crystallite size was calculated from X-ray line broadening by using the Scherrer equation with the Warren's correction (*16*).

The reduction of catalysts was studied with a commercial thermogravimetric system (Cahn 113). The percent reduction was quantified from the weight loss during reduction as well as the weight gain during a subsequent oxygen treatment at 673 K. The exact procedure was presented elsewhere (*17*).

Chemical characterization. The catalysts were reduced *in situ* in flowing hydrogen prior to chemisorption and reaction studies. The procedure for hydrogen adsorption, ethane hydrogenolysis, and carbon monox-

TABLE 1

Physical Characteristics of Supports

Support	Loading of Nb_2O_5 (wt%)	BET surface area (m^2/g SiO_2)
SiO_2	0	300
Nb_2O_5–SiO_2, one monolayer (NSI)	29.3	377
Nb_2O_5–SiO_2, two monolayers (NSII)	48.3	378
Nb_2O_5–SiO_2, three monolayers (NSIII)	59.3	382
SiO_2, blank[a]	0	330

[a] See text for the procedure of the blank run.

ide hydrogenation have been described in detail before (*13, 17*). Briefly, pulsed chemisorption was done in a Quantasorb unit. The kinetic studies were run with a stainless-steel microreactor equipped with an on-line gas chromatograph for product analysis. The reactor was operated in a differential mode at atmospheric pressure.

RESULTS

Niobia–Silica Supports

Table 1 shows the niobia loading and BET surface area of the three niobia–silica supports prepared in this study. A notation has been adopted in which NS denotes the Nb_2O_5–SiO_2 surface phase oxide and the Roman numeral represents the number of monolayers of niobia on silica. For example, NSII was prepared by depositing another monolayer of Nb_2O_5 onto NSI. It should be noted that the surface areas were reported on a per gram SiO_2 basis; the areas on a per gram sample basis were less. When compared on the same basis, the NSI support had a 26% larger surface area than SiO_2. One reason for this increase could be the desorption of water during the thermal treatments in our preparation. To examine this possibility, a SiO_2 sample was treated with an identical procedure in the absence of niobium(V) ethoxide. The resulting increase in surface area was not as large as that found for NSI. The blank run thus ruled out thermal effects as the sole factor in changing the surface area. Interestingly enough, there was no further increase in the BET surface areas of the NSII and NSIII supports after the deposition of more niobia.

Figure 1 shows the X-ray diffraction results of the three NS supports. The diffractograms of NSI and NSII were indistinguishable from that of amorphous SiO_2 alone. There was a broad peak (at $2\theta \sim 20$–$30°$) for NSIII, but still no diffraction peaks of Nb_2O_5 were found. The lack of diffraction peaks suggested that the deposited Nb_2O_5 phase was well dispersed as crystallites smaller than 2–3 nm in diameter (which is the detection limit for Mo radiation due to line broadening) or amorphous.

The uniformity of the deposited Nb_2O_5 phase was further investigated with TEM. Figures 2a and b correspond to TEM micrographs of bulk SiO_2 and Nb_2O_5, respectively. The Nb_2O_5 sample appears to be more opaque because of its stronger interaction with the electron beam. In fact, the difference in electron density between SiO_2 and Nb_2O_5 could be used in identifying any maldistribution of Nb_2O_5 on SiO_2. Figure 2c is a typical micrograph of the NSI sample. The image was similar to that of SiO_2, and showed no heterogeneity which would correspond to the presence of large Nb_2O_5 particles. The distribution of the Nb_2O_5 phase

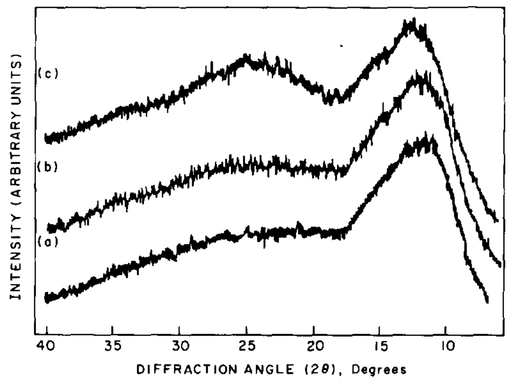

FIG. 1. X-Ray diffractograms (Mo$K\alpha$) of niobia–silica surface phase oxides: (a) one monolayer, (b) two monolayers, and (c) three monolayers of niobia.

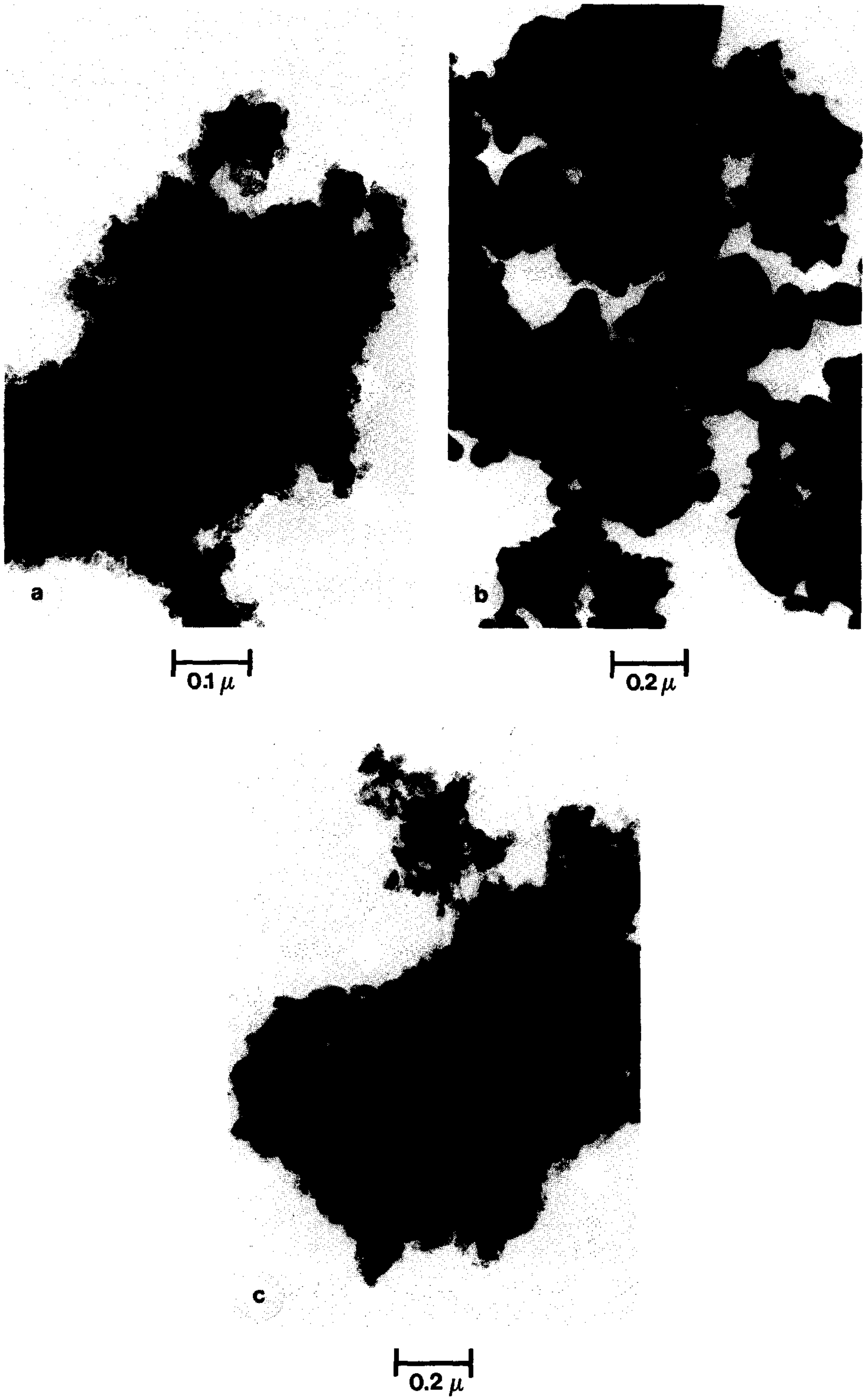

FIG. 2. TEM micrographs of (a) Davison 952 SiO_2, (b) Nb_2O_5 prepared in Ref. (*17*), and (c) NSI prepared in this study.

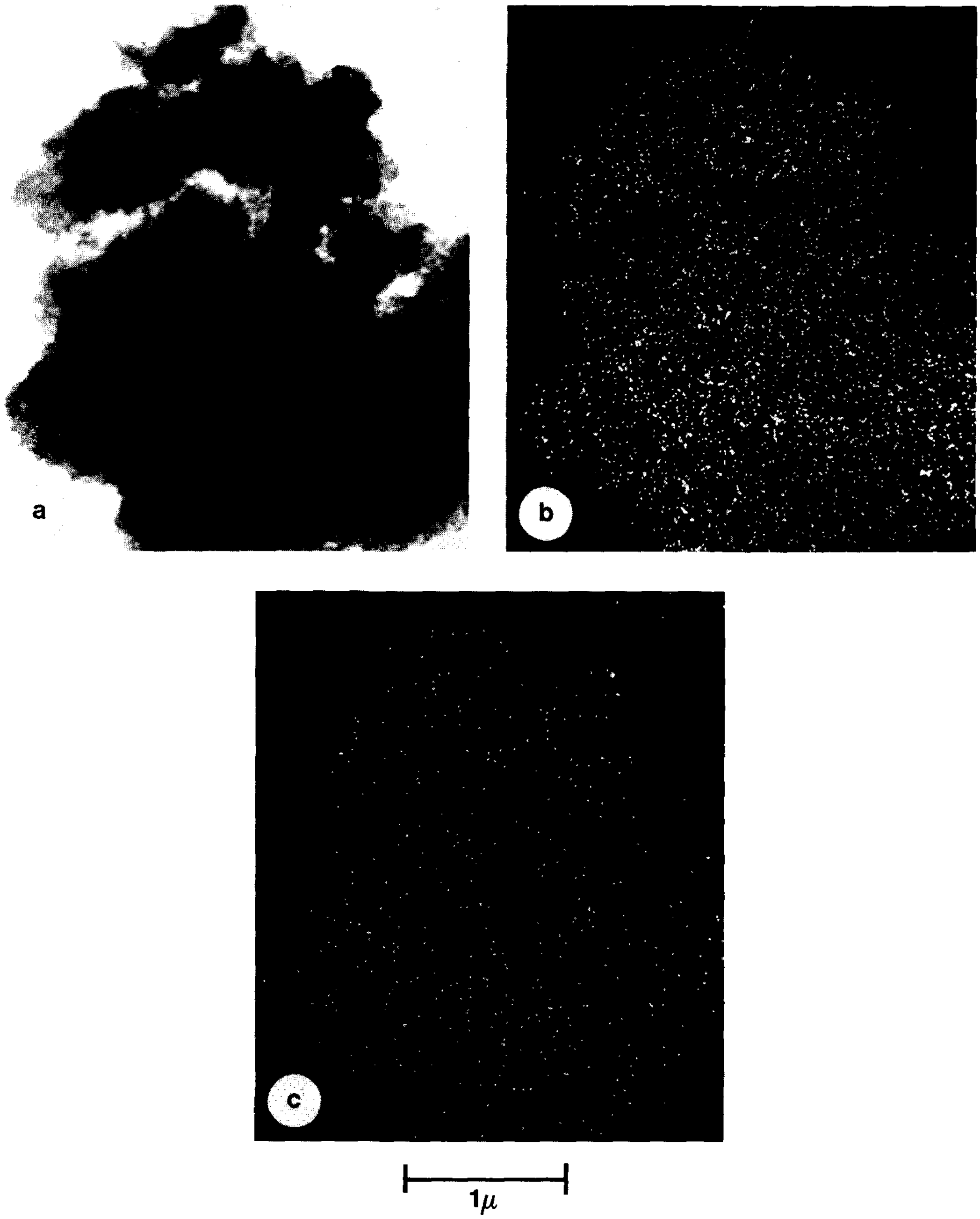

FIG. 3. X-Ray energy dispersive analysis of the NSI support: (a) TEM micrograph of the image region, (b) Si map, and (c) Nb map.

was also probed by energy dispersive analysis. Figures 3b and c show the elemental mapping of Si and Nb, respectively, in the sample region represented in Fig. 3a. A good correspondence could be seen between the Si and Nb maps. However, the study of a large number of samples revealed that in some sample regions the distribution of Nb_2O_5 was less than uniform. This was particularly true for the NSIII support.

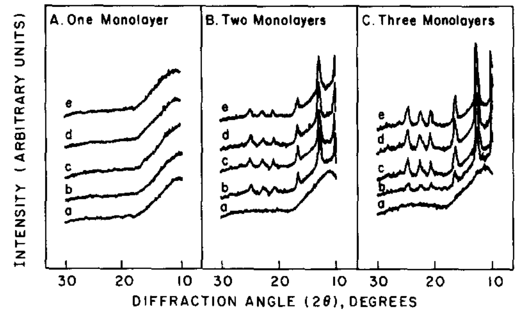

FIG. 4. X-Ray diffractograms showing the sintering behavior of niobia–silica surface phase oxides heated in air at 873 K for (a) 0 h, (b) 2 h, (c) 4 h, (d) 8 h, and (e) 16 h. (A) one monolayer, (B) two monolayers, and (C) three monolayers.

Figure 4 shows the X-ray diffraction patterns of the NS supports after they had been calcined in air at 873 K for up to 16 h. A significant difference in behavior was found between the NSI sample and the other two samples. NSI was stable under the thermal treatment, as suggested by no change in the diffractogram (Fig. 4A). By contrast, diffraction peaks corresponding to Nb_2O_5 evolved for both the NSII and NSIII supports after heating for 2 h or longer (Figs. 4B and C). The high-temperature treatment (873 K for 16 h) led to about a 20% loss of the original BET surface area for all three supports.

Adsorption and Reaction Behavior

The study of chemical reactivity was limited to a nickel catalyst prepared with NSI, which had been shown to be the only support stable under all pretreatment conditions to be used for the catalyst. In order to compare the data in this study with those previously reported for Ni/Nb_2O_5 catalysts, two specific reduction treatments were used. Table 2 lists the physical parameters of the catalysts. The weight loading, percent reduction, and crystallize size were combined to determine the total number of surface nickel atoms, which was subsequently used in calculating turnover frequencies as done previously (*13*).

TABLE 2

Physical Characteristics of Ni/NSI Catalysts

Reduction treatment	% Reduction[b]	Average crystallite size[c] (nm)
(9, 573, 1)[a]	30	3
(9, 773, 1)	100	6

[a] (9, 573, 1) represents a 9 wt% sample reduced at 573 K for 1 h.

[b] Determined by thermogravimetric measurements.

[c] Determined by X-ray line broadening.

TABLE 3

Pulse Chemisorption Data for Supported Nickel Catalysts

Catalyst	Reduction treatment	No. of H atom/Surface Ni atom
Ni/NSI	(9, 573, 1)	0.29
Ni/NSI	(9, 773, 1)	0.14
Ni/Nb_2O_5[a]	(10, 573, 1)	0.16
Ni/Nb_2O_5[a]	(10, 773, 1)	0.02

[a] Taken from Ref. (*17*).

Tables 3–5 show the results of hydrogen chemisorption, ethane hydrogenolysis, and CO hydrogenation for the Ni/NSI catalysts reduced at 573 and 773 K for 1 h.[2] Evidence of metal–support interaction was found from the suppression in hydrogen chemisorption and in ethane hydrogenolysis activity in comparison with Ni/SiO_2 catalysts (*10*). The suppression was more severe for the sample reduced at the higher temperature, yet another characteristic of SMSI. In the case of CO hydrogenation, the Ni/NSI catalyst also behaved similarly to Ni/Nb_2O_5 catalysts in three main features (*13*): a higher activity than Ni/SiO_2 (*18*), a shift in product distribution toward more hydrocarbons higher than methane, and a production of olefins. Table 6 shows a few typical runs of the Ni/NSI (9, 573, 1) sample to illustrate the latter two points.

The above results establish that the niobia–silica surface phase oxide is indeed

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[2] Results for a more severe reduction treatment are also included in Table 5 and will be discussed later.

TABLE 4

Kinetic Results for Ethane Hydrogenolysis over Supported Nickel Catalysts

Support	Reduction treatment	E_A[a] (kJ/mole)	n[b]	m[b]	Activity at 478 K (molecule/s/surface Ni atom)
NSI	(9, 573, 1)	179	0.9	−1.7	5.9×10^{-5}
NSI	(9, 773, 1)	172	0.9	−1.7	4.1×10^{-6}
Nb_2O_5[c]	(10, 573, 1)	183	0.9	−1.7	4.9×10^{-6}
Nb_2O_5[c]	(10, 773, 1)	170	1.0	−0.9	1.4×10^{-7}

[a] Determined from the temperature dependence of the rate r_0, at ethane and hydrogen partial pressures of 0.03 and 0.2 atm, respectively.

[b] Exponents in the experimental power rate law, $kp_E^n p_H^m$, where p_E and p_H correspond to partial pressures of ethane and hydrogen, respectively.

[c] Taken from Ref. (*13*).

an interacting support for nickel. For a comparison with the bulk Nb_2O_5 support our previous results of a 10 wt% Ni/Nb_2O_5 catalyst (*13, 17*) are included in Tables 3 to 5. Under identical reduction treatments, the niobia-supported catalysts exhibit a larger suppression in hydrogen chemisorption and in ethane hydrogenolysis activity. It should be noted that the Ni/Nb_2O_5 catalyst, with a larger average crystallite size (9 nm), should be less interacting than catalysts with smaller crystallites if all other parameters remain the same (*13, 19*). The above comparison thus clearly indicates that niobia is a more interacting support than niobia–silica. Another measure of the extent of SMSI is a hierarchy developed on the basis of the three chemical probes used in this study (*13*). Table 7 compares the ranking of niobia- and niobia–silica-supported nickel catalysts in terms of the five stages in this hierarchy. It is again apparent that niobia is the more interacting support of the two.

DISCUSSION

Preparation and Characterization of the Support

As shown by XRD and TEM, the procedure used in this study to deposit mono-

TABLE 5

Kinetic Results for CO Hydrogenation over Supported Nickel Catalysts

Support	Reduction treatment	Activation energy (kJ/mole)		Turnover frequency at 548 K ($\times 10^{-2}$ s^{-1})	
		E_{CH_4}	E_{CO}	N_{CH_4}	N_{CO}
NSI	(9, 573, 1)	104	122	6.3	37
NSI	(9, 773, 1)	114	122	3.8	17
Nb_2O_5[a]	(10, 573, 1)	123	123	2.4	6.3
Nb_2O_5[a]	(10, 773, 1)	116	112	1.8	5.8
NSI	(9, 873, 16)	104	111	1.5	4.6
Nb_2O_5	(10, 873, 16)	116	133	0.4	1.1

[a] Taken from Ref. (*13*).

TABLE 6

Product Distribution for a 9 wt% Ni/NSI Catalyst Reduced at 573 K for 1 h

Temperature (K)	Flow rate (liters/h)	CO conversion (%)	Hydrocarbon distribution (mole %)					Olefin/paraffin ratio		
			C_1	C_2	C_3	C_4	C_5	C_2	C_3	C_4
460	1.2	2.2	58.4	20.8	12.8	4.8	3.2	0	0.48	0.28
474	1.2	4.8	60.5	16.3	13.2	6.6	3.4	0	0.22	0.37
474	1.8	3.2	61.1	16.6	12.5	6.5	3.3	0	0.33	0.40

layers of niobia did not result in bulk Nb_2O_5 crystallites distributed heterogeneously over the substrate. However, both of these characterization techniques have limitations and do not provide direct evidence of the uniform spreading of the deposited phase at an atomic level. As such evidence would be difficult to obtain, a qualitative argument in favor of a homogeneous Nb_2O_5 surface phase will be presented on the basis of our data and related literature results.

Recently, Gliński and Kijeński (*20*) reported the preparation of vanadium–alumina and vanadium–silica oxides with vanadyl isobutoxide as a precursor. These authors found that the reaction between alkoxides and surface hydroxyls is very sensitive, and that the distribution of the deposited metal ions correspond to the distribution of hydroxyls on the original silica surface. Since we used a very similar procedure, it is reasonable to expect that the deposited niobium precursor is distributed uniformly over silica after the impregnation.

TABLE 7

Extent of SMSI as Ranked by the Hierarchy Developed in Ref. (*13*)

Catalyst	Reduction treatment	Extent of interaction
Ni/NSI	(9, 573, 1)	A mild stage III
Ni/NSI	(9, 773, 1)	Stage III
Ni/Nb_2O_5[a]	(10, 573, 1)	Stage III
Ni/Nb_2O_5[a]	(10, 773, 1)	Stage V

[a] Taken from Ref. (*13*).

As XRD detected no Nb_2O_5 peaks even after the NSI sample had been heated at 873 K for 16 h, apparently niobia produced from the niobium precursor during calcination remained uniformly distributed and wetted the silica substrate. It is believed that the observed increase in BET surface area occurred as a result of this calcination and wetting step.

The spreading of a metal oxide over an oxide substrate is consistent with the low surface tensions of oxides, as noted by Ruckenstein (*21*). In his analysis of the thermodynamics of wetting, Ruckenstein further pointed out that a very thin film with a thickness of a monolayer or less can wet the substrate, but the film is no longer stable if it exceeds a critical thickness. The latter point brings to mind the sintering behavior of the NSII and NSIII supports. It appears that these two samples are not thermodynamically stable, so that heating at 873 K overcame the kinetic barrier and led to the growth of Nb_2O_5 crystallites. Some particle growth might have already occurred in the NSIII sample during the milder calcination at 773 K for 2 h in the normal preparation procedure, as indicated by the diffuse diffraction feature (Fig. 1c) and the heterogeneity noted in the TEM study of this sample (see Results).

The difference in sintering behavior between NSI and the other two supports is strong, though still indirect, evidence that Nb_2O_5 was well dispersed as a monolayer surface phase oxide in this sample. Then it is important to ascertain whether it is valid to assume a 16-Å^2 unit mesh in calculating the weight loading. This is a difficult question, since the structure of the surface phase oxide and the niobia–silica interaction are both unknown. Crawford and Anderson (*22*) pointed out that all the niobium oxide family of compounds have crystal structures of the ReO_3 type. Within each block of the ReO_3 structure, the niobium atom positions are about 3.9 Å apart. In crystallized MoO_3, another crystal with a similar structure, the surface area of a MoO_3 unit is taken to be 15.4 Å^2 (*23*). Our value of 16 Å^2 for each $NbO_{2.5}$ unit is thus consistent with these observations. It is estimated that our surface coverage of niobia is no more accurate than 20 ± 10%, especially in view of the increase in BET surface area during preparation. This uncertainty could account for the TEM observation that when a large number of samples were examined, some appeared to be less homogeneous. However, if the fraction of silica surface covered by the deposit of the first niobia layer were low, then one would have expected a further increase in the BET surface area with the deposit of subsequent layers as more silica surface became wetted. As shown in Table 1, there is no increase in the BET surface area beyond the NSI support. This observation together with other data reinforce the notion that the first niobia layer indeed spreads homogeneously over most of the silica substrate.

Chemical Behavior of the Support

The Ni/NSI catalyst used in this study exhibited SMSI characteristics with respect to three chemical probes. It is not surprising that a monolayer of niobia was sufficient to induce such behavior. The key prerequisite for SMSI, according to the current understanding, is the presence of a reduced oxide species on the metal surface. One monolayer of niobia on our silica substrate has a surface area of about 240 m^2/g catalyst, which is more than enough to cover the nickel crystallites in a 9 wt% nickel catalyst. (Assuming each nickel crystallite is a cube with five faces exposed, the total nickel surface area is about 8 m^2/g catalyst.) So there is a sufficient supply of niobia, as long as the niobia–silica interaction is not strong enough to prevent the migration. Furthermore, our results rule out bulk oxide reduction as a necessary condition for SMSI (*24*), since there is no bulk niobia in our system.

If the supply of Nb_2O_5 is plentiful in Nb_2O_5–SiO_2 from the standpoint of available area, then we have to reason why it is not as interactive as Nb_2O_5 under identical reduction treatments. Although we could not totally rule out the possibility of some nickel crystallites sitting on uncovered SiO_2 contributing to the chemistry, we believe such an effect to be small for reasons given above. Instead, we suggest the lower availability of Nb_2O_5 in the surface phase oxide to be responsible for the difference in behavior. At present it is unclear whether the migration of oxide to the metal surface is by diffusion through or over the crystallite (*7*, *12*). In either case the supply of diffusing oxide species is practically limitless in bulk Nb_2O_5. But in Nb_2O_5–SiO_2, the diffusion of the initial species would leave behind a "bare" surface with SiO_2 exposed. The remaining niobia is further away from the metal crystallites. It also becomes more difficult to be reduced, since the reduction would be facilitated by hydrogen spillover from the active metal (*25*). These effects could combine to make the Nb_2O_5–SiO_2 support less interacting. We recently reported similar results for a TiO_2–SiO_2 surface phase oxide support (*26*), which suggest the same general mechanism of interaction for titania and niobia.

In order to further examine the above model, we subjected the Nb_2O_5- and Nb_2O_5–SiO_2-supported nickel catalysts to a much more severe reduction treatment. Table 5 shows the results for CO hydrogenation after a reduction at 873 K for 16 h for these two catalysts. Both samples exhibited a decline in activity with little variation in the product distribution. The Ni/Nb_2O_5 (10, 873, 16) sample had the lower activity of the two and in fact, the lowest activity of all the niobia-supported nickel catalysts. Magnetic studies (*27*) showed that this sample exhibited a loss of metallic nickel and an apparent decrease in its average crystallite size from 8 to 5 nm. As discussed elsewhere (*27*), these results are interpreted as the formation of a compound between the migrating oxide and some of the nickel atoms. In contrast the Ni/NSI (9, 873, 16) catalyst showed a much less significant change in either the amount of metallic nickel or the crystallite size in magnetic studies. The magnetic and kinetic results together argue in favor of our suggestion that by limiting the availability of niobia, the niobia–silica support is less interacting even under the most severe reduction treatment used. The chemical significance is that nickel catalysts on the less interacting niobia–silica support show a higher CO hydrogenation activity than those supported on niobia under all reduction conditions used.

SUMMARY

This study showed that it is possible to prepare a surface phase niobia on silica, which is an interacting support for nickel catalysts. The surface phase oxide is not as interacting as bulk niobia and, under the most severe reduction treatment used, does not suffer a large loss in CO hydrogenation activity. This system thus represents a feasible approach to manipulate metal–support interactions. Furthermore, surface phase oxides should prove useful in studying SMSI in general.

Although this work focused only on the chemistry of the one-monolayer support, the preparation of two and three monolayers of niobia revealed some interesting behavior of the surface phase oxides. There seems to be a critical concentration (thickness) below which the deposited phase wetted the substrate, but above which it sintered into crystallites at high temperatures. The characterization of similar oxide–oxide systems, which are expected to have interesting properties either as catalysts or supports, deserves further attention.

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