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Properties of Ni/SiO_2 Catalysts: Relationship to Ether Formation from Alcohols

L. S. KRAUS,[1] HERMAN PINES,* AND J. B. BUTT[2]

*Department of Chemical Engineering and *Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3120*

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The objective of this study was better understanding of the relationships among structural, chemical, and physical properties of Ni/SiO_2 and ether formation in the reaction of alcohols. The primary reactions investigated were those of the conversion of 1-butanol at 1 atm, 160°C and conversion <25%. Further characterization of catalyst acidic/metallic properties was conducted with 1,1-dimethylcyclopropane at 80°C. X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of Ni in the various catalysts. Two series of catalysts were investigated: 0.7, 2.7, 4.7, and 8.5 wt% Ni/SiO_2 prepared by precipitation of basic $NiCO_3$ on the silica, and 4.8 and 6.0 wt% Ni/SiO_2 prepared by neutral impregnation with nickel nitrate. Various pretreatment and reduction conditions were investigated; for the 0.7–8.5% series it was found that the temperature of drying prior to reduction/reaction was an important variable. For the 8.5% catalyst, temperature of reduction also became an important factor. Study of the ether formation activities for various catalysts from both series, in conjunction with XPS investigation and 1-1 dimethylcyclopropane reactivity, indicated that the active site for ether formation is an acidic nickel silicate promoted by Ni(0). Ether formation is inversely related to surface-reduced Ni on these catalysts, thus it does not appear that large ensembles of zero-valent nickel play a significant role in the catalysis. © 1991 Academic Press, Inc.

INTRODUCTION

Ether formation from alcohols over reduced, supported, or unsupported metal catalysts is a reaction not often mentioned in the literature, but has been observed to occur with many different metals including Ni, Pt, Ir, Pd, and Rh (*1*). We think the reaction is novel because ether formation is generally thought of as occurring with amphoteric metal oxides or with homogeneous or heterogeneous acidic catalysts (*2*), not with metals.

However, there is no doubt that alcohol–ether reactions do occur over typical metal catalysts. The questions thus have to do primarily with (i) how the physical characteristics of the catalysts, such as metal dispersion, or extent of reduction relate to activity and ether formation selectivity, and (ii) the nature of the active site for ether formation. The present objective is to address these two questions via study of a graded series of Ni/SiO_2 catalysts.

LITERATURE

Ni in a number of forms has been used before in alcohol conversion studies (*1, 3–11*). Conditions vary but supported catalysts have normally been prepared via precipitation of basic nickel carbonate from a solution of aqueous nickel nitrate onto whatever support was employed. The conversion of *primary alcohols* in the presence of hydrogen over Ni catalysts in the temperature range of 100–200°C results in a product distribution attributed to reductive dehydroxylation of the alcohol to an alkane, the ether

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[1] Present address: Amoco Oil Corporation, P.O. Box 3011, Naperville, IL 60566.

[2] To whom correspondence should be addressed, at the Department of Chemical Engineering.

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formation/dehydroxylation of the alcohol and dehydrogenation. In addition, there is the possibility of decarbonylation of the aldehyde formed in the last step. Under similar conditions *secondary alcohols* undergo rapid equilibration to ketones, reductive dehydroxylation, and ether formation, but tertiary alcohols only undergo reductive hydroxylation (*1*). With Ni catalysts, primary alcohols are less reactive overall and more selective for ether formation (*9–13*). Under the same conditions secondary alcohols are ca. 5× more reactive than sterically similar primary alcohols.

The activity and selectivity of Ni catalysts seem to be greatly affected by the reaction conditions employed. For both 1° and 2° alcohols, overall conversion increases 3× as the temperature is increased from 130 to 190°C yet ether formation selectivity decreases by 25% (*1*). Use of He decreases both conversion and ether selectivity at the same temperatures (*6*). The presence of alkali on Ni catalysts decreases both conversion and ether selectivity up to an order of magnitude (*1, 3, 4, 7, 10, 14*), as do bases such as ammonia and pyridine (*1, 3, 6*). Thus these materials are very sensitive to basic poisoning. Prior work indicates that the active site is mostly related to the extent of reduction, both for supported Ni (*3, 11*) or others (*6, 12–15*).

Extent of reduction. For Ni the extent of reduction has a critical effect both on alcohol conversion activity and ether selectivity. Unreduced He-calcined 7% NiO/SiO_2–Al_2O_3 is inactive for ether formation whereas an identical catalyst, reduced in H_2 at 450°C is active for alcohol conversion with high (90%+) ether selectivity (*11*). Optimal selectivity for ether appears at NiO reduction of 98–99%, with lower reduction (97%) favoring dehydrogenation and higher (>99%) favoring dehydroxymethylation. Thus, a "nearly reduced" Ni was indicated as preferable for ether selectivity. However, separate studies of the reducibility of NiO indicate that essentially 100% reduction is obtained under conditions such as H_2, 450°C (*16–19*), so the participation of partially reduced species in preferential ether formation remains open to question.

Structure sensitivity. The conversion of alcohols to ethers over reduced Ni catalysts is apparently structure-sensitive in several ways, particularly with regard to catalyst and reactant structure. Little work has been done on characterization of metal catalysts for ether formation reactions. For Ni a generalization is that <1.0 wt% (small particles) and >10.0 wt% (large particles) have lower specific activity for alcohol conversion and ether formation than those intermediate. On the other hand, the structure-sensitivity of ether formation has been illustrated by comparison of Ni and NiCu catalysts (*14*). Decreasing the number of large Ni ensembles via alloying with Cu depresses ether formation. This brings forward questions concerning (i) the effect of the size of Ni ensembles and (ii) the effect of reduction on the size.

The steric nature of an alcohol is also important. As the degree of branching increases both reactivity and selectivity decrease (*1–8*), possibly due to the proximity of branching with respect to an hydroxyl group (*8*).

Mechanistic proposals. A mechanism for ether formation has been proposed previously (*1, 3–13*). This envisions concerted *trans*-elimination steps over acidic and basic sites where the acidic site is an unreduced transition metal ion and the basic site is an oxide ion. Reaction with an acidic site forms a carbenium ion-like intermediate, while that with a basic site an alkoxide-like intermediate, which then reacts to form ether and water product molecules. Support for this view is found experimentally. Reduced Ni/SiO_2 adsorbs both NH_3 and HCl to a greater extent than SiO_2 alone (*21*), giving rise to enhanced Lewis acid/ammonia and OH bands in IR spectra. Ether formation is inhibited both by alkali poisons on acid sites and by basic molecules (NH_3, etc.), but they affect metal-catalyzed reactions such as dehydrogenation to a much lesser extent (*1–3*). Further in reaction studies of 2,2-dimethyl-1-propanol and *cis*- and *trans*-1,4-cyclohexanediol (*1–13*) there is a significant influence of the reactant configuration on ether formation. Mechanisms based on a fully developed carbenium ion do not work; but all cases yield to the general acid–base analysis so we use the term "carbenium ion-like" above to describe the intermediate.

Overall, results obtained with supported Ni conform well with the acid–base hypothesis (*22–24*), which requires some unreduced NiO for formation of the basic site. However, some workers (*16–18*) report that 100% reduction of unsupported Ni gives the most active catalysts. Further, the activities of reduced, unsupported catalysts do not accord well with any envisioned NiO content (*3*).

Other mechanistic proposals, based on studies with Ni, NiCu, Pt/SiO_2, $PtAu/SiO_2$, and $PtCu/SiO_2$ (*14, 15*) envision metal ensembles as required for ether formation. For a number of reasons (*25, 26*) this seems unlikely, but such an approach is also tested in the present study.

EXPERIMENTAL

Two basic experiments were carried out, the first for 1-butanol to dibutyl ether over Ni/SiO_2 catalysts prepared by precipitating basic nickel carbonate onto an inert silica support, and the second for conversion of 1,1-dimethylcyclopropane to neopentane and isopentane on reduced, partially reduced, and unreduced Ni/SiO_2. All reaction experiments were carried out in a standard flow microreactor, using a continuous flow saturator feed system for 1-butanol and a pulse feed system for dimethylcyclopropane, with hydrogen carrier gas in both cases. Reactor temperatures of 80–450°C were used with reproducibility of ±2°C. Typical conditions employed were ca. 0.1 g catalyst with a reaction gas mixture flow (sc) of 10 cm^3/min and alcohol to H_2 ratio of 1/10 (*M*), for 1-butanol, or a pulse size of ca. 2–10 into 100 cm^3/min H_2 for dimethylcyclopropane. Reaction temperatures were 160 and 80°C, respectively. Details on experimentation are reported by Kraus (*20*).

XPS measurements employed a VG Scientific ESCALAB/SIMSLAB apparatus, interfaced with a Packard–Bell IS/VT 286 computer for data acquisition. This was equipped with a high-pressure reactor stage which allowed *in situ* pretreatment of the catalyst sample and transfer to the XPS system without atmospheric exposure.

Catalysts. All catalysts were prepared with Davison Grade 62 SiO_2. The inertness of this material for alcohol conversion was verified independently (*20*). The same batch of silica was used in preparation of all catalysts.

Two sets of catalysts were produced:

(i) Precipitation catalysts: 0.7, 2.7, 4.7, and 8.5 wt% Ni/SiO_2, prepared by precipitating basic nickel carbonate onto the silica.

(ii) Impregnation catalysts: 4.8 and 6.0 wt% Ni/SiO_2, prepared by impregnating the silica with aqueous nickel nitrate to incipient wetness. The average uncertainty limits of metal content are ±1.3% of the value of wt% reported.

Reagents. The He and H_2 used as pretreatment and carrier gases were UHP (99.999%) grade from Linde. Both were further purified by passing through a reduced 10 wt% Mn/SiO_2 trap to remove oxygen and then a 4A trap at liquid N_2 temperature to remove water. The CO was Research (99.97%) grade from Linde, also purified by passage through Mn/SiO_2 and 4A traps, the latter at dry ice/acetone temperature. The 1-butanol was from Aldrich Chemical Co, no. 15,467-0, spectrophotometric grade, 99+%, Lot LP 05916HP. The 2-methyl-2-propanol was also from Aldrich, no. B8,592-7, 99.5%, Lot TP01412PP. The 1,1-dimethylcyclopropane was from Wiley Organics, no. 1310.50, 99%. The *n*-hexane used to dilute this was from Aldrich, no. 13,938-6, 99+%, Lot MT 03026KT. The purities of

TABLE 1A

Extent of Reduction Data; $T_R = 350°$

Catalyst	T_D (°C)	H_2 (consumed at 350°C (moles)[a]	Percentage reduction
0.7% Ni	125	$6.25 + 10^{-8}$	0.26
2.7% Ni	125	$4.63 + 10^{-7}$	0.50
	350	$2.88 + 10^{-7}$	0.31
4.7% Ni	125	$1.29 + 10^{-6}$	0.81
	350	$9.39 + 10^{-7}$	0.59
8.5% Ni	125	$6.33 + 10^{-5}$	21.8
	350	$2.57 + 10^{-5}$	8.9

[a] Measured value; range of 25–50% of value given is estimated.

TABLE 1B

Extent of Reduction Data; Variable T_R

Catalyst	T_D (°C)	T_R (°C)	Consumption of H_2 at T_R (moles)[a]	Percentage reduction
8.5% Ni	350	275	0.68×10^{-5}	2.4
	350	315	1.31×10^{-5}	4.5
	350	350	2.57×10^{-5}	8.9

[a] Measured value; range of 25–50% of value given is estimated.

all reagents were confirmed by gas chromatography.

RESULTS AND DISCUSSION

Relationship between Ni/SiO$_2$ Structure and Ether Formation from 1-Butanol

The results below are primarily for the Ni/SiO$_2$ series prepared by precipitation. In all cases the catalysts were subjected to the following pretreatment: drying in He, 125 or 350°C (T_D), 2h; reduction in H_2 (T_R), 275–350°C, 2h; cooling in flowing H_2 to reaction temperature. The reaction conditions were 160°C,[3] atmospheric pressure with a feed of 1/10 1-butanol/H_2 and typical space velocities of 100 cm^3 feed/min-g cat. The selectivities are reported as (moles alcohol converted to ether/total moles alcohol converted) × 100.

Physical characterization. The extent of reduction and exposed metal surface area were determined using temperature-programmed reduction (TPR) and hydrogen–deuterium exchange (HDE), respectively.

In the TPR experiments the catalyst after drying (Ar) was cooled in flowing Ar to −65°C and reduction commenced with a H_2/Ar : 5/95 mixture from −65°C to 700°C at 8°C/min (linear). The results are shown in Table 1 for experiments with 0.200 g catalyst and reduction gas flow rate of 30 cm^3/min. As the weight loading increases, the amount of H_2 consumed to 350°C increases, the extent of reduction increases, and the rate of hydrogen consumption maximum noted for $T < 350°C$ (see Fig. 1) shifts to lower temperatures. These extents of reduction observations are consistent with prior reports (*27, 28*). The majority of the Ni in these catalysts reduced at high temperatures with the rate of H_2 consumption maximum at 580–680°C. The difficulty in reduction is well known (*22–24*). A typical TPR history is shown in Fig. 1. The two regions of reduction indicate two types of Ni species in the unreduced catalysts. The low-temperature peak goes to nickel carbonate weakly interacting with the support, while the high-temperature peak indicates some carbonate with much stronger interaction. It has been observed that as metal loading increases the opportunity for direct contact between precipitate and support decreases and the quantity of weakly interacting material increases.

HDE experiments to determine surface area were conducted in a constant volume recirculating reactor system that also could be operated in a flow-through mode. Details of the experiments are given in Ref. (*20*). The surface areas so determined are given in Table 2.

Activity and selectivity: Effect of pretreatment. Both the temperature of prereduction drying, T_D, and of reduction, T_R, have an influence. In all cases, however, the reactions were very clean (only dibutylether and propane products) and, with the exception

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[3] Results over a range of temperatures 50°C from 160° were found to be similar.

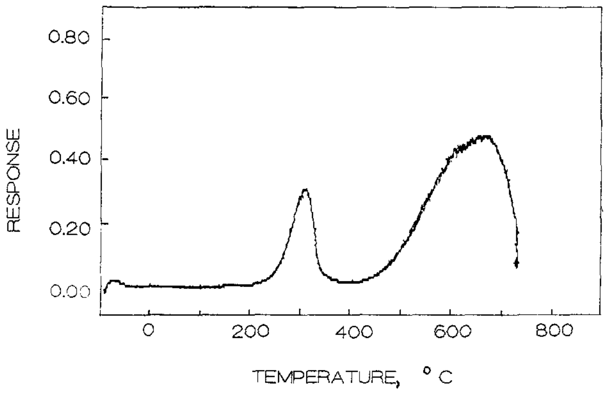

FIG. 1. TPR spectrum for 8.5% Ni/SiO_2, T_D = 350°C.

of the 0.7% catalyst, obtain steady activities and have very stable ether formation, as shown in Fig. 2 for the 8.5% catalyst. Figure 2 also indicates that a higher drying temperature in catalyst preparation results in significantly lower activity but has no effect on selectivity. This was observed for all catalysts save 0.7%, where activity was essentially unaffected by T_D.

Increased T_D might lead to increased support interaction, decrease in the reducibility of the metal, and decrease in the amount of exposed, unreduced metal (*24*). Thus, loss of activity could be due to diminished quantities of either reduced Ni or surface, unreduced Ni. Since the measured quantities of surface-reduced metal are not significantly different for catalysts dried at either temperature the loss of ether formation activity may be associated with loss of accessible, unreduced Ni. However, since the product selectivities are roughly the same for both values of T_D it seems more likely that there is a proportionate decrease in the amounts of both reduced and unreduced Ni at higher T_D. The absence of any significant effect of T_D on the 0.7% catalyst is ascribed to a higher degree of interaction between metal precursor and support for very low loadings (*22–24*).

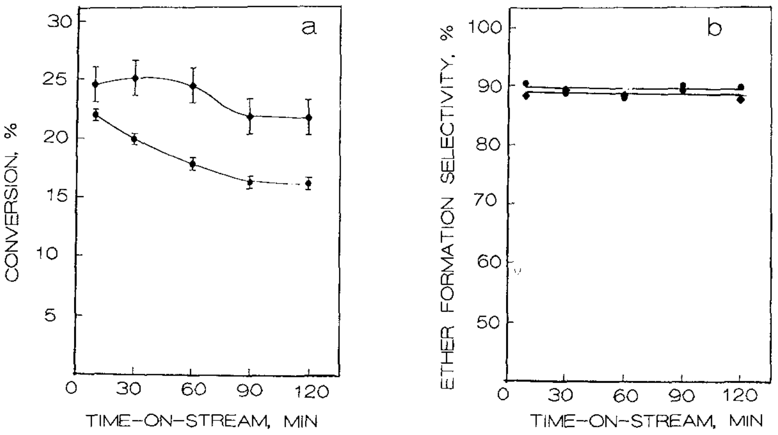

FIG. 2(a). 1-Butanol conversion vs time-on-stream; (b) ether formation selectivity vs time-on stream. Conditions: 8.5% Ni/SiO_2; reaction at 160°C, T_R = 350°C. (◆) T_D = 125°C; (●) T_D = 350°C.

TABLE 2

Metal Surface Area Data[a]

Catalyst[b]	T_D (°C)	Surface reduced Ni (moles)[c]
0.7% Ni	125 or 350	$5.95 + 10^{-7}$
2.7% Ni	125 or 350	5.06×10^{-6}
4.7% Ni	125 or 350	8.01×10^{-6}
8.5% Ni	125 or 350	1.45×10^{-5}

[a] In all surface area measurement experiments T_R = 350°.

[b] Sample size = 0.200 g.

[c] Based on 1/1 : H/Ni stoichiometry and negligible uptake on unreduced Ni.

The effect of reduction temperature, T_R, was studied for the 8.5% catalyst. Samples were dried in He at 350°C and then reduced in H_2 at 275, 315, or 350°C. The results are shown in Fig. 3. Both activity and selectivity increase with T_R; indeed, the sample reduced at 275°C had no selectivity for ether formation and propane was the only product. It is clear that T_R is critical in producing a catalyst with either formation activity and that this is not merely a thermal effect. There is no simple requirement for a certain, critical amount of reduced metal on the catalyst. If this were the case then the 8.5% catalyst dried at 350°C and reduced either at 275 or 315°C should have been more active than the 2.7% catalyst dried and reduced at 350°C, since the former contains larger amounts of reduced metal. Similar comparisons pertain to other catalyst pairs.

Correlations between activity/selectivity and metallic species. The data of interest here are ether formation activities in terms of (1) total Ni loading, (2) total reduced Ni present, (3) surface-reduced Ni present, and (4) unreduced Ni present.

The relationship between catalyst metal loading and overall activity is shown in Figs. 4a and 4b for initial and steady-state (2 h time-on-stream) conditions; corresponding results for ether formation activity are similar (*20*). The conversion numbers can be normalized with respect to the total Ni (reduced and unreduced) present. In both cases the 0.7 and 2.7% catalysts have much higher initial activities than the others, with the 2.7% catalyst exhibiting better activity maintenance after 2 h; both trends are independent of T_D. Thus, it would appear that there is an optimal metal loading for reaction in the vicinity of 2.7%, as discussed subsequently.

The relationship between the initial rate of ether formation normalized with respect to the *total* reduced Ni present is given in Fig. 5.[4] Ether formation activity does not correlate with the total amount of reduced Ni present; in fact, there is a near-inverse relationship between them. A more useful comparison is provided by activity vs surface-reduced metal since it is the latter which is accessible to a reactant. For this the percentage exposed reduced metal must be known. From the data of Tables 1 and 2 it is seen that for the 0.7 and 4.7% catalysts the upper limit for the number of moles of reduced Ni (TPR, ±50%) can be 1.5–3.0 times smaller than the lower limit for the number of moles of surface, reduced Ni. For the 2.7% catalyst the measured lower limit for surface-reduced Ni is about 2.5–5.0 times greater than total reduced Ni. Since there cannot be more reduced Ni than the total, it is concluded that the dispersions of reduced metal in these catalysts are very high. Consequently, for 0.7, 2.7, and 4.7% catalysts the reduced metal percentage exposed is taken to be 100. On the same basis for 8.5% the apparent percent exposed is 10. These results in terms of initial rate of ether formation per surface-reduced Ni are shown in Fig. 6. As the amount of surface, reduced Ni increases the rate of ether formation per exposed Ni decreases for either T_D used.

A conclusion from Fig. 6 is that the large reduced-metal ensemble mechanism for ether formation is probably not correct. If it were, then one would certainly expect an increase in ether formation per surface

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[4] In this figure and Fig. 6 the data points moving left to right for a given T_D correspond to the 0.7, 2.7, 4.7, and 8.5% catalysts, respectively.

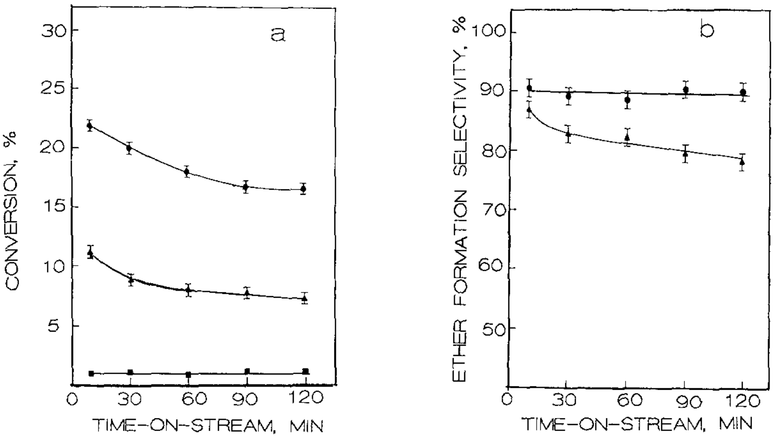

FIG. 3(a). 1-Butanol conversion vs time-on-stream at different reduction temperatures; (b) ether formation selectivity vs time-on-stream at different reduction temperatures. 8.5% Ni/SiO_2, reaction at 160°C, T_D = 350°C. (■) T_R = 275°C; (▲) T_R = 315°C; (●) T_R = 350°C.

metal atom as the number of surface metal atoms increases, correlated to increasing metal loading (*27, 28*). The steady-state rate of ether formation (*20*) also shows that the small metal ensemble catalysts are more active than the large ensemble (8.5%) material. Correlation of ether formation rates, in terms of total unreduced Ni present results in plots that look very similar to Fig. 4, basically because the extents of reduction are so small that the amounts of total and unreduced Ni are nearly the same. There is no direct correlation of activity with unreduced metal.

In summary, for Ni/SiO_2 prepared by precipitation of basic $NiCO_3$ onto silica, the following general trends are observed for 1-butanol reaction:

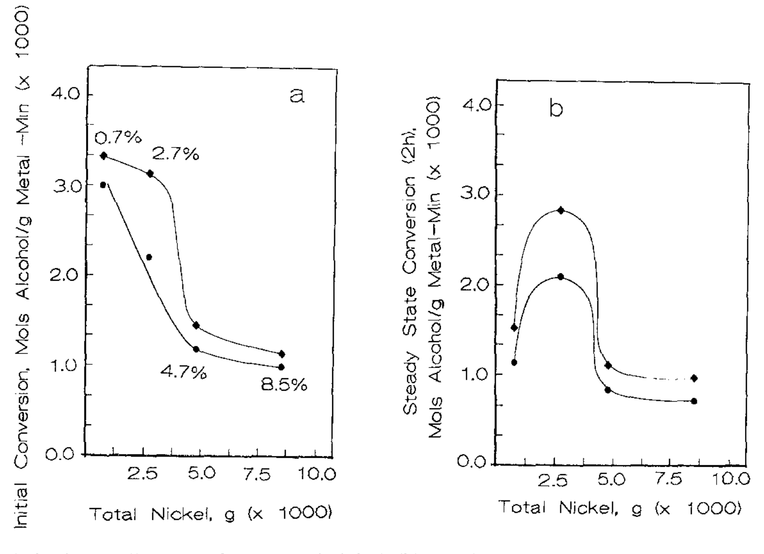

FIG. 4(a). Initial overall conversion vs total nickel; (b) steady-state conversion (at 2 h) vs total nickel. T_R = 350°C; reaction at 160°C. (◆) T_D = 125°C; (●) T_D = 350°C.

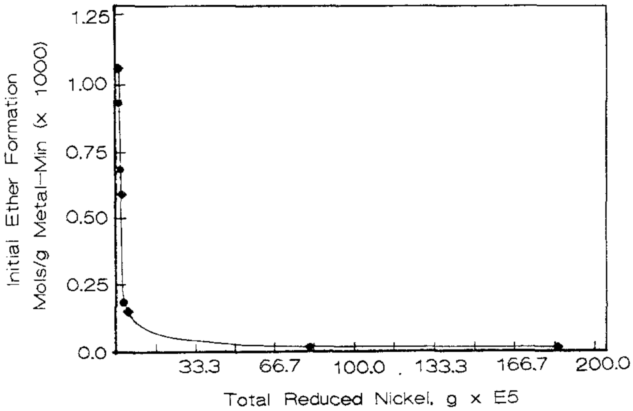

FIG. 5. Initial rate for ether formation vs total reduced nickel. T_R = 350°C; reaction at 160°C. (◆) T_D = 125°C; (●) T_D = 350°C.

(1) The prereduction drying temperature has a significant effect on both total and ether formation activity, but little effect on ether selectivity. The loss in activity at higher drying temperature is possibly due to a loss in surface-unreduced Ni.

(2) The temperature of reduction is important with lower reduction temperatures giving lower ether activity and selectivity.

(3) There is an apparent optimal metal loading for these catalysts in the vicinity of 2.7 wt%.

(4) The lack of correlation between ether formation activity and the amount of surface, reduced Ni present makes the large metal ensemble mechanism seem very unlikely.

(5) The lack of correlation of ether formation activity with the amount of unreduced Ni present also casts doubt as to whether this species is active for the reaction.

Active Species for Ether Formation

The roles of reduced and unreduced Ni in ether formation are explored by (1) following the reactivity behavior of reduced, unreduced, and partially reduced catalysts, (2) probing the acid/metal functionality of both

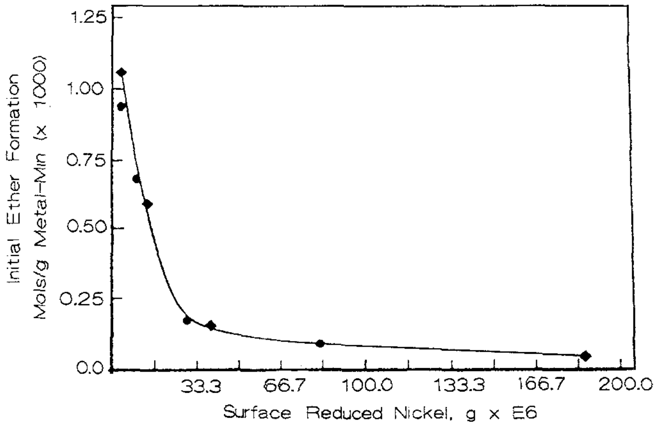

FIG. 6. Initial ether formation vs surface reduced nickel for reaction at 160°C. Conditions as for Fig. 5.

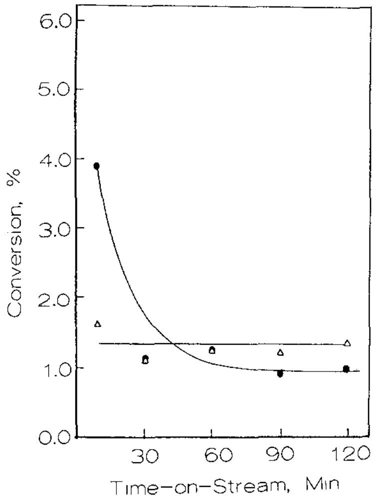

FIG. 7. 1-Butanol conversion vs time-on-stream for reduced Ni at 160°C. T_R = 450°C; T_C = 450°C. (●) 6.0% Ni/SiO_2 (C); (△) 4.8% Ni/SiO_2 (NC).

active and inactive catalysts with the reaction(s) of 1,1-dimethylcyclopropane, and (3) looking at surface species via XPS.

Reactivity Behavior

Primarily reduced Ni. The catalysts employed were prepared by impregnation from aqueous nickel nitrate. A 4.8-wt% sample, uncalcined, and a 6.0-wt% sample, calcined, were employed. Both were pretreated *in situ* prior to reaction in H_2, 450°C, 2h and then cooled in H_2 to reaction temperature. Such Ni/SiO_2 catalysts are easily reduced (*29*), with uncalcined materials essentially 100% reduced after the above pretreatment, and even calcined materials reduced to 75–90% (*18, 30, 31*). For the calcined 6.0-wt% sample of this study, the extent of reduction was confirmed to be 82% via TPR (*20*). On this basis, reduction of the 4.8% catalyst was taken to be 100%. Reaction conditions were as described previously, except that a nominal space velocity of 50 cm^3 feed/min-g cat was employed.

Conversion results are shown in Fig. 7. For the 4.8% catalyst selectivity was always 100% for propane formation, while for the 6.0% catalyst selectivity changed from 65% ether to 35% propane at 10 min to a steady value of 100% propane. For reduction temperatures from 200–450°C neither catalyst was active for ether formation, and only slightly active for dehydrogenation/decarbonylation. It follows that highly reduced Ni is a poor ether formation catalyst and is not responsible for any ether formation noted; thus the unreduced Ni of the 6.0% may play some role in ether formation.

Partially reduced and unreduced Ni. The catalyst employed for this study was the 8.5% Ni/SiO_2. Prior to reaction the fresh samples were pretreated *in situ* by one of the following two methods:

(1) Drying, He, 350°C, 2 h
(2) Reducing, H_2, 350°C, 2 h
(3) Purging He, 350°C, 15 min
(4) Cooling He, 350°C – 75°C, 45 min
(5a) H_2, 75°C, 18 h
(5b) CO, 75°C, 18 h
(6) Purging, He, 75°C, 15 min
(7) H_2, 300°C, 2 h
(8) Cooling, H_2, 300°C reaction temperature, 0.5 h

Catalysts were prepared using either step 5a or 5b, pretreatments A and B, respectively.

Pretreatment A results in a catalyst containing both reduced (~9%) and unreduced Ni (cf. Table 1). Pretreatment B results in a catalyst that contains predominantly unreduced Ni, since the CO treatment forms volatile nickel tetracarbonyl readily removed in subsequent steps (*22–24*); unreduced Ni does not form the tetracarbonyl (*32–33*). From metal analysis pretreatment B is approximately 10–15% of the Ni content, in rough agreement with that expected from the extent of reduction. The two pretreatments are identical as far as severity and duration of thermal treatments. Additional details are given in (*20*).

Conditions of reaction were as before for the 8.5% catalyst and conversion results are shown in Fig. 8. Pretreatment A catalyst shows relatively high activity, with ether selectivities of 91.8, 88.5, 86.7, 88.3, and 87.9% at 10, 30, 60, 90, and 120 min, respec-

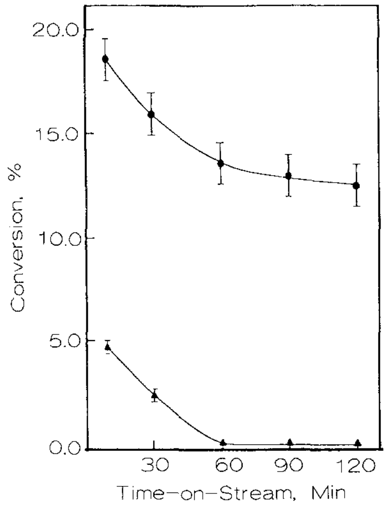

FIG. 8. 1-Butanol conversion vs time-on-stream for 8.5% Ni/SiO_2 at 160°C. T_D = 350°C; T_R = 350°C. (▲) CO treatment (T = 75°C); (●) no CO treatment.

tively. The acivity for pretretment B catalyst was much lower and ether detected in significant amounts only at 10 (85.4%) and 30 (78.7%) min. Propane was the only other product in all cases. Thus removal of reduced Ni decreases the overall activity for alcohol conversion and eliminates selectivity for ether formation. The final "activity" of catalyst B is essentially zero. These results strongly suggest involvement of zero-valent Ni, either present in the active site or in concert with the active site.

Reactions of 1,1-Dimethylcyclopropane

This molecule is a useful probe of both the acidic and metallic character of supported Ni. The possible reactions (*34*) produce neopentane (2,3 ring opening) and isopentane (1,2 ring opening) via metallic (*35, 36*) and acidic sites (*37*), respectively. Isobutane is also sometimes seen via a 1, 2 ring opened species from a metal-catalyzed reaction to form isobutane and methane.

The major results of the pulse reaction experiments with dimethylcyclopropane (*20*) show that for the 4.8 and 6.0% catalysts (produced by neutral aqueous impregnation) the neopentane/isopentane ratio ranges roughly from 10 to 40 for all pulse sizes. This indicates that these materials are much more metallic than acidic in nature (acidity is attributed to unreduced Ni). For the 8.5% catalyst produced by basic precipitation, the neopentane/isopentane ratios are 4–11, indicative of significantly greater intrinsic acidity. Comparison of the neopentane/($i - C_4 + i - C_5$) ratios for the three catalysts leads to a similar conclusion. Methane was generally produced in amounts equal to isobutane. Overall, these results show that acidity is required for ether formation. The precipitation catalyst is favored because of higher Ni–SiO_2 interaction, resulting in a higher fraction Ni unreduced and corresponding higher acidity.

The validity of attributing isobutane formation to the acidic function was investigated separately via pyridine poisoning. After an experiment with a 10.0-μl pulse on the 8.5% material, a 0.25-μl pulse of pyridine was introduced, then another 10-μl reactant pulse. After pyridine only very small amounts of isopentane and isobutane were detected, and neopentane/($i - C_4 + i - C_5$) was 2.4 (the neopentane before and after pyridine treatment was approximately the same); overall selectivity behavior approached that of the 4.8–6.0% catalysts.

A further experiment was run using the 8.5% pretreatment B catalyst. The only reaction product formed was isopentane supporting the view that all zero-valent Ni is removed by the CO treatment. However, since isopentane, not isopentene, was observed the catalyst has hydrogenation activity even in the absence of Ni(0). Hydrogenation activity of this type has been ascribed to heterolytic dissociation of H_2 on Lewis acid–base sites for alumina (*34*), although the adsorption of H_2 on oxidized Ni is rather weak (*38, 39*).

These results help explain some of the prior data on ether formation. It was seen earlier that CO extraction results in a catalyst with initial ether formation ca. 3.5 times less than its unextracted counterpart (Fig. 8). Further, in the dimethylcyclopropane experiments the conversion to acid-catalyzed products is about 4 times smaller for CO-treated material than for untreated material (*20*). Exact comparisons cannot be made because of different experiments, but qualitatively it seems clear that catalysts with the most acidity have the highest ether formation activity. The reason for the decrease in acidity upon CO treatment is not obvious. The technique was chosen because previous work (*22–24*) had reported the method to result in catalysts without Ni(0) but unchanged otherwise. Possibly the presence of Ni(0) enhances the effectiveness of the acidic sites; other studies indicate that isobutane is a primary reaction product, thus it must come from a concerted reaction of the dimethylcyclopropane over metallic *and* acidic sites. Interaction with acidic sites is also possible in the absence of metal, but the numbers are diminished (i.e., 8.5% Ni/SiO_2 with all Ni(0) removed still has some ether formation activity). This is not to claim that metallic Ni exclusively is the active site in ether formation but the evidence is that Ni(0) could at the least have some synergistic relationship with unreduced, acidic Ni. Such a possibility accords with both the 1,1-dimethylcyclopropane and ether formation data.

A final experiment with the pretreatment A catalyst was run with H_2 reduction at 275°C rather than 350°C. Comparison showed that the higher temperature of reduction resulted only in slightly greater acidity (based on neopentane/$(i - C_4 + i - C_5)$ from dimethylcyclopropane), so even the lower reduction temperature gives material with both acidic and metallic character, and this dual characteristic is not a strong function of reduction temperature.

XPS Studies

X-ray photoelectron spectroscopy is useful for characterization of unsupported NiO and Ni/SiO_2 catalysts (*30, 31, 40–45*). For NiO there are distinct chemical shifts for Ni(0), Ni(+2), and Ni(+3) species. For Ni/SiO_2 neutral, aqueous impregnation gives catalysts containing NiO that is only weakly interacting with SiO_2 (*30, 31, 43*) and is easily reduced to Ni(0). By contrast, basic ion exchange or basic precipitation give Ni(+2) species that interact strongly with SiO_2 (*31, 46*). The most useful characterization of Ni/SiO_2 via XPS appears to be via the position of the Ni $2p_{3/2}$ and O $1s$ peaks. Table 3 gives a convenient summary of these compiled from a number of sources.

Experiments were done with 6.0% Ni/SiO_2 and also with the pretreatment A and B catalysts (8.5% Ni/SiO_2). To review, these represent cases of predominately reduced Ni, both reduced and unreduced Ni, and only unreduced Ni, respectively. Results of the XPS are given in Table 4. In the Ni $2p$ spectrum for 6.0% Ni/SiO_2 peak maxima are observed at 852.1 and 869.0 eV;[5] the lower E_B peak can be assigned to the Ni $2p_{3/2}$ peak of Ni(0) and the higher to Ni $2p_{1/2}$ of Ni(0) (*45*). In the O $1s$ spectrum the major peak at 532.6 eV is characteristic of oxide ions in Ni/SiO_2 prepared using basic precipitation techniques, i.e., $NiSiO_3$ and SiO_2. Since the neutral aqueous impregnation technique was used for this catalyst, and extensive silicate formation is not expected (*22–24*), this is attributed to oxide ions in the silica. The Si $2p$ spectrum shows one major peak at 103.9 eV. While this is somewhat higher than the upper end of the usual binding energy range for Si $2p$ there appears to be no special significance to this.

For 8.5% Ni/SiO_2 there are maxima in the Ni $2p$ at 856.0 and 873.3 eV, respectively, both with a satellite peak at +5.9 eV. These are attributed to Ni $2p_{3/2}$ and $2p_{1/2}$, respectively. Also, for the $2p_{3/2}$ peak there is a distinct shoulder on the low energy side which, when deconvoluted from the main peak, has a corrected maximum at 852.1 eV. The peaks at 856.0 and 852.1 eV indicate that Ni(0) and some species of unreduced Ni are both present, and the 3.9 eV shift of

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[5] In general, sample charging was measured and corrected using the displacement of the C $1s$ binding energy peak from 285.0 eV. See Table 4.

TABLE 3

XPS Peak Positions Useful for Characterization of Ni/SiO_2

	Peak position (eV)	References
Ni $2p_{3/2}$		
Ni(0)	852.4–852.9	*(40–43, 45–50)*
Ni(II): NiO	854.0–854.9	*(40–42, 46–49)*
Ni(II): Ni/SiO_2[a]	854.7–854.9, 856.0–856.1	*(30, 31, 43)*[c]
Ni(II): Ni/SiO_2[b]	856.3–857.0	*(31, 45, 46)*
Ni(II): $Ni(OH)_2$	855.5–856.6	*(40, 42, 45, 46, 49)*
Ni(III): Ni_2O_3	855.7–856.1	*(40, 42, 46, 49)*
Ni(II): $NiSiO_3$	856.7	*(46)*
Ni(II): Antigorite	855.6–855.7	*(45)*
O 1S		
O^{2-}: NiO	529.1–530.0, 531.4–531.7	*(40–42, 46–50)*
O^{2-}: Ni/SiO_2[a]	532.1–532.2, 533.0–533.1	*(31, 43)*
O^{2-}: Ni/SiO_2[b]	532.5, 532.8–533.0	*(31, 46)*
O^{2-}: $Ni(OH)_2$	531.0–532.0	*(40, 42, 46, 49, 50)*
O^{2-}: Ni_2O_3	530.9–531.8	*(40, 42, 47, 48)*
O^{2-}: $NiSiO_3$	532.5	*(46)*
O^{2-}: antigorite	531.1–531.5	*(45)*
O^{2-}: SiO_2	532.6	*(46)*

Note. Reference positions: Si 2*p*: 102.9–103.6 eV; C 1*s*: 284.9–285.1 eV.

[a] Ni/SiO_2 from neutral, aqueous impregnation.

[b] Ni/SiO_2 from basic precipitation or ion exchange.

[c] NiO in Refs. *(30, 31)* determined to be bulk, crystalline form. Peak positions for Ni reported are somewhat higher than those reported elsewhere.

the shoulder peak indicates that the unreduced Ni peak cannot be attributed to NiO, which has only a 1.5–2.4 eV chemical shift, as discussed below. The maximum in the O 1*s* spectrum at 532.2 eV is not characteristic of either NiO or SiO_2, but may arise from some other type of Ni compound. In general, these spectra are not surprising since this catalyst is difficult to reduce. Further, since NiO is known to reduce in H_2 at temperatures less than the 350°C used with this catalyst *(16–19)* it would be expected that the unreduced Ni species present is *not* NiO.

For the 8.5% Ni/SiO_2 which has had its Ni(0) removed with CO, the Ni 2*p* maxima are at 855.7 and 872.9 eV, each with a satellite at +5.9 eV. In contrast to the unextracted 8.5% material, this catalyst has no low energy shoulder on the Ni $2p_{3/2}$ peak which provides further confirmation of the absence of Ni(0). The position of the Ni $2p_{3/2}$ peak is +3.6 eV higher than expected for Ni(0). The O 1*s* maximum at 532.0 eV is reasonably attributed to oxide ions other than those in the silica support and also indicates that the unreduced Ni species is not NiO. The Si 2*p* peak at 103.6 eV is typical of the Si 2*p* value for SiO_2.

The Ni $2p_{3/2}$ peaks for the two 8.5% catalysts can be attributed to $Ni(OH)_2$, Ni_2O_3, or Ni-silicate ($NiSiO_3$ or Ni-antigorite). Also the O 1*s* peak positions could be attributed to oxide ions in any of these three Ni compounds. $Ni(OH)_2$ can be eliminated as a possibility because it decomposes even in nonreducing atmospheres to NiO at 300°C *(51)*, and is reduced to Ni(0) at 200°C *(22)*. Thus

TABLE 4

XPS Experimental Data; Corrected E_B, eV[a]

Peak	6.0% Ni/SiO_2[b]	8.5% Ni/SiO_2[c]	8.5% Ni/SiO_2–(CO)[d]
Ni $2p_{3/2}$	852.1[e]	856.0[f,g]	855.7[g]
Ni $2p_{1/2}$	869.0[e]	873.3[g]	872.9[g]
O 1*s*	532.6	532.2	532.0
C 1*s*	285.0	285.0	285.0
Si 2*p*	103.9	103.9	103.6

[a] Referenced to C 1*s* = 285.0 eV; −9.8 (6.0), −9.5 (8.5), −9.5 (8.5 − CO).

[b] Pretreatment: H_2, 450°C, 2 h.

[c] Pretreatment: He, 350°C, 2 h; H_2, 350°C, 2 h (analogous to pretreatment A).

[d] Pretreatment: He, 350°C, 2 h; H_2, 350°C, 2 h; CO, 75°C, 18 h; H_2, 300°C, 2 h (analogous to pretreatment B).

[e] Low-intensity satellite peak at +6.0 eV.

[f] Significant shoulder at 852.1 eV.

[g] Significant satellite peak at +5.9 eV.

the inert (He, 350°C) and reduction (H_2, 350°C) treatments either alone or in combination should remove any $Ni(OH)_2$. Similar factors pertain to Ni_2O_3. While this is not a stable bulk compound (*25*), it is stabilized on NiO surfaces (*40–42, 48, 52*). However, it is also reduced quantitatively to Ni(0) in H_2 at 300°C (*53*), so it is very unlikely to survive the 350°C, H_2 treatments of present work. Indeed, heating in vacuum at 350°C is sufficient to decompose Ni_2O_3 quantitatively (*54*).

This leaves the silicate. Nickel silicate ($NiSiO_3$ or Ni antigorite) has Ni $2p_{3/2}$ and O 1*s* peak positions very similar to those observed with the 8.5% Ni/SiO_2 catalysts. It is also well known that catalysts prepared using the pretreatment conditions and basic precipitation method used here contain large amounts of nickel silicate after reduction (*22–24*). Thus, it seems most likely that the unreduced Ni species in these catalysts is a form of nickel silicate.

Some intercomparisons. There is qualitative agreement among the XPS results and data from the 1,1-dimethylcyclopropane studies. The 6.0% Ni/SiO_2 catalyst was found via XPS to contain predominately Ni(0), while the cyclopropane reaction over this catalyst gave a product distribution favoring the metal-catalyzed product neopentane. XPS data also showed for extracted 8.5% Ni/SiO_2 the absence of Ni(0); the corresponding cyclopropane reaction gave a product distribution containing the purely acid-catalyzed ring opening product, isopentane. The unextracted Ni/SiO_2 gave product distributions intermediate to these two catalysts.

Comparison of XPS results with ether formation data is also informative. The 6.0% Ni/SiO_2 with predominately Ni(0) had minimal ether formation. Also, the 8.5% Ni/SiO_2 extracted with CO contained *only* Ni silicate and demonstrated some activity for ether formation, so the silicate plays some role as a site for this reaction. Finally the untreated 8.5% Ni/SiO_2, containing both silicate and Ni(0) was the most active for ether formation, indicative of a synergism between Ni(0) and silicate in ether formation.

CONCLUSIONS

Several conclusions, based on the combination of ether formation, dimethylcyclopropane reaction, and XPS studies are:

(1) An active species for ether formation from 1-butanol in Ni/SiO_2 catalysts is acidic nickel silicate.

(2) Ni(0) enhances the acidic properties and ether formation activity of Ni silicate.

(3) The prereduction drying temperature (T_D) has a significant effect on both the ether formation and alcohol conversion activity of Ni/SiO_2; however, ether formation selectivity is relatively unaffected. Higher T_D decreases ether formation activity and this may be due to a decrease in the accessible surface area of the Ni silicate present.

(4) Reduction temperature (T_R) also plays a major role in the ether formation activity of Ni/SiO_2. There are a number of possible reasons for this (decrease in Ni(0) with decrease in T_R, variation in acidity with T_R are examples) but the data do not point to one predominate effect.

(5) There is an apparent optimal metal loading of Ni on SiO_2 for both overall alcohol conversion and ether formation activity.

In the present work the 2.7% Ni/SiO_2 demonstrated higher activity than any of the other catalysts investigated. This may be due to a higher fraction exposed of the nickel silicate, since the decreasing extent of reduction with decreasing Ni loading observed in TPR indicates a larger fraction of silicate in the 2.7% catalyst vs the 4.7% or 8.5%. While 0.7% Ni/SiO_2 had a very high initial activity, rapid deactivation occurred and the 2.7% Ni/SiO_2 is clearly better long-term. It is also possible that at this level of nickel loading there is an optimum interaction among silicate, Ni(0) and dispersion; however, we know of no good way to examine this in direct experiment.

(6) The active site for ether formation in Ni/SiO_2 is not a large ensemble of zero-valent Ni. An inverse correlation between metal surface area and ether formation activities was observed, opposite to that expected if ether formation occurred over large zero-valent Ni ensembles.

(7) While silicate is apparently active for ether formation there seems no direct correlation with silicate content. This is due at least in part to the acidity-enhancing cooperative effect between Ni silicate and zero-valent Ni. Possible reasons for this are that different catalysts have different amounts of Ni silicate accessible to reactants and the acidic nature of the silicate in the type of catalyst changes with the metal loading.

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