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Preparation, Reduction, and Chemisorption Behavior of Niobia-Supported Nickel Catalysts

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Two niobia(Nb_2O_5)-supported nickel catalysts, containing 2 and 10 wt% nickel, were prepared by incipient wetness impregnation. Subsequent to reduction in hydrogen at 573 and 773 K for 1 h, these catalysts adsorbed a smaller amount of hydrogen at room temperature than silica-supported nickel catalysts similarly prepared. The suppression in hydrogen adsorption was more pronounced for the 2 wt% sample, which had a smaller average crystallite size as determined by X-ray line broadening measurement. Thermogravimetric analysis showed a facile reduction of the nickel precursor salt to metallic nickel. The chemisorption behavior was thus ascribed to strong metal-support interactions (SMSI). These results compared with similar data previously obtained for titania(TiO_2)-supported nickel catalysts showed that niobia was a more interacting support than titania for nickel, when parameters such as average crystallite size and reduction treatment were comparable. The extent of interaction appeared to correlate with the reducibility of the oxide support, although quantitative thermogravimetric measurements suggested that the amount of support being reduced was small.

1. INTRODUCTION

It is well documented that the chemical behavior of a supported metal catalyst can be influenced by metal-support interactions (*1, 2*). Several years ago Tauster *et al.* (*3*) reported a particularly strong kind of interaction for TiO_2-supported group VIII noble metals. They found a significant suppression of both hydrogen and carbon monoxide chemisorption on these catalysts subsequent to a reduction at 773 K. Since the encapsulation of metal particles and the poisoning of impurities are insufficient to explain such a suppression, these authors inferred the existence of a strong metal-support interaction (SMSI).

The work of Tauster *et al.* has since prompted many studies on the chemical and physical characterization of TiO_2-supported metal catalysts. For example, their catalytic properties of ethane hydrogenolysis (*4, 5*), CO hydrogenation (*6, 7*), and the hydrogenation of hydrocarbons (*8, 9*) have been investigated. In general, TiO_2-supported metal catalysts, with their unique chemisorption behavior, also display different activity and selectivity compared to catalysts on a non-interacting support such as silica. The physical properties of these catalysts have been studied by techniques including X-ray photoelectron spectroscopy (*10, 11*), Mössbauer spectroscopy (*11*), and electron spin resonance spectroscopy (*12, 13*). Results from these studies point to a consistent, though incomplete, model of SMSI catalysts, in which interaction is related to the reduction of the oxide support and the subsequent electron transfer between the support and the metal.

An empirical correlation between SMSI effects and support reducibility was in fact found by Tauster and Fung (*14*). By monitoring the hydrogen chemisorption behavior of iridium supported on a number of oxides, these authors reported that several binary oxides which are easily reduced exhibit SMSI behavior. However, relatively little attention has been paid to these other

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TABLE 1

Loss of Support Surface Area as a Function of Calcination Temperature

Calcination temperature (K)	Percentage loss[a]
753	18.1
773	19.6
793	47.1
813	76.9

[a] Percentage loss was calculated by comparing the BET surface area after and before calcination.

oxides, compared to the rigorous research activities on TiO_2-supported catalysts.

In an attempt to provide further insight into the SMSI effect, we have selected one of these oxides, niobia (Nb_2O_5), and completed a chemical characterization of niobia-supported nickel catalysts. In this paper reduction and chemisorption data will be presented with the emphasis on the effects of crystallite size, reduction treatment, and support reducibility. Reaction results with ethane hydrogenolysis and CO hydrogenation will be reported later (*15*).

2. EXPERIMENTAL

2.1. Sample Preparation and Treatment

The Nb_2O_5 support was prepared by following the procedure suggested by Tauster and Fung (*14*) with slight modifications. A methanolic solution was prepared by adding 20 g of niobium(V) chloride (Aldrich, 99.8% pure) to 1 liter of methanol (Fischer, A.C.S. reagent grade). Ammonium hydroxide (Fischer, A.C.S. reagent grade) was then introduced dropwise into the solution until the pH increased abruptly to a final value which was between 6 and 6.5. The white precipitate was filtered and washed several times with distilled water. After being dried in an air oven at 380 K overnight, several batches of the support material were calcined in flowing oxygen (50 ml/min at STP) at different temperatures for 2 h. As shown in Table 1, the BET surface area of the support decreased with increasing calcination temperature from 753 to 813 K. The BET surface area of the oxide prior to calcination varied from batch to batch, and ranged from 18 to 39 m^2/g. X-Ray diffraction showed only a crystalline Nb_2O_5 phase for all samples calcined over this temperature range. The support used for the catalysts in this study was calcined at 793 K, and had a BET surface area of ca. 10 m^2/g.

Two batches of Ni/Nb_2O_5 catalysts, containing 2 and 10 wt% nickel, were prepared by the incipient wetness impregnation with an aqueous solution of nickel nitrate hexahydrate. Prior to reduction at different temperatures, these samples were dried overnight in an air oven at 400 K. The average nickel crystallite size, as determined by X-ray ($MoK\alpha$) line broadening measurement on the sample reduced at 773 K, was 4(±1) and 9(±1) nm for the 2 and the 10 wt% catalyst, respectively. The metal loadings were confirmed by atomic absorption (AA) measurement, after having dissolved nickel from the reduced catalyst with nitric acid.

Gases used in this study for sample treatment were of 99.99% purity or better (Airco Industrial Gases). Hydrogen and nitrogen were further purified by a deoxo unit (Englehard Industries) and an O-sorb (Scientific Gas Products), respectively, before passing through a molecular sieve trap (Union Carbide, Linde 5A). Oxygen was passed directly through a molecular sieve trap.

2.2. Thermogravimetry (TG)

The reduction of Ni/Nb_2O_5 catalysts was studied by using a commercial thermogravimetric system (Cahn 113). Both the decomposition of the nickel salt in nitrogen and the reduction in hydrogen were monitored. In a typical run about 50 mg of sample was loaded into the balance, the sample weight was then recorded as a function of temperature in a flowing stream of nitrogen or hydrogen (40 ml/min at STP). The system had a microprocessor to control the furnace, so that the sample could be heated with a linear temperature ramp or held at a constant temperature for a specified period. The oxidation of a reduced catalyst was studied in the same system by heating the sample to 673 K in a flowing stream of oxygen (40 ml/min at STP). All data reported here have been corrected for buoyancy and drag with blank runs.

2.3. *Chemisorption*

Pulse chemisorption and temperature-programmed desorption (TPD) experiments were done in a commercial Quantasorb unit (Quantachrome Corp.). The unit included a thermal conductivity detector to measure the concentration of hydrogen in a flowing nitrogen stream. The response of the detector could be monitored directly with a recorder and the area under a particular eluted peak was measured by a built-in integrator. The unit had been modified such that the heating of the sample cell was controlled by an external temperature programmer.

In a typical run, 0.2–0.3 g of sample was heated in flowing hydrogen with a linear increase of temperature (12 K/min) from room temperature to the final reduction temperature. After reduction the sample was cooled to room temperature *in flowing hydrogen*. Nitrogen was then used to purge the sample cell, and a temperature-programmed desorption run was done to desorb any adsorbed hydrogen. A pulse chemisorption experiment was performed after the sample had again cooled to room temperature. The pulse chemisorption procedure was similar to that described by Wanke *et al.* (*16*). A calibration was first established by measuring the detector response to a hydrogen pulse of known volume injected into a line bypassing the sample. Pulses of hydrogen (0.1 ml per pulse) were then allowed to pass through the sample cell every 4 min. This was continued until the eluted peaks became constant, indicating no further irreversible uptake.

After the pulse chemisorption, the sample was exposed to flowing hydrogen (50 ml/min at STP) at room temperature for 1 h. A second TPD-pulsed chemisorption cycle was then carried out. Each catalyst was thus subjected to two complete desorption–adsorption cycles following reduction. As discussed below, an interesting difference was found between the two desorption cycles for the Ni/Nb_2O_5 catalysts.

3. RESULTS AND DISCUSSION

3.1. *Decomposition and Reduction Behavior*

The reduction behavior of Ni/Nb_2O_5 catalysts was studied by two different approaches. In the first approach, the temperature of the sample was increased at a rate of 10 K/min from room temperature to 573 K in a stream of flowing nitrogen, and held at 573 K until the sample weight was constant. The weight loss data, in terms of the percentage of initial weight and temperature versus time, are shown in Fig. 1a for the 10% Ni/Nb_2O_5 catalyst. Most of the weight loss had occurred by the time the sample temperature reached 573 K, and the decomposition was complete after about 30

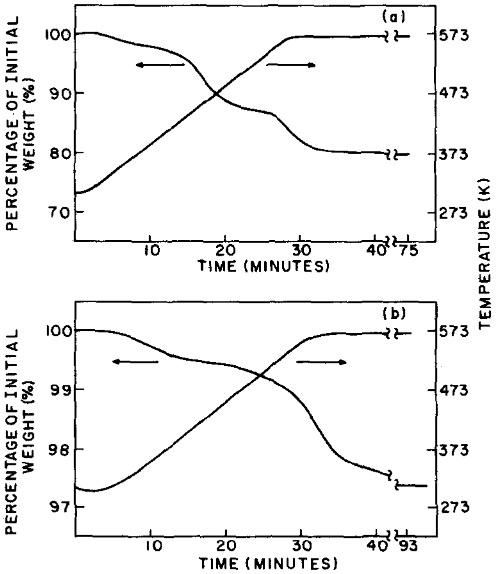

FIG. 1. Thermogravimetric data for the treatment of a 10 wt% Ni/Nb_2O_5 catalyst. (a) Decomposition in nitrogen. (b) Reduction in hydrogen.

min at 573 K. During this step the nickel salt decomposed into nickel oxide (NiO), as confirmed by X-ray diffraction.

After the nitrogen treatment the sample was cooled to room temperature, exposed to a stream of flowing hydrogen, and heated by following the temperature schedule as used before. The reduction of nickel oxide to metallic nickel was then monitored by recording the percentage weight loss as a function of time. As shown in Fig. 1b, most of the weight loss occurred during the heating step and the weight of the sample became constant after it had been held at 573 K for 1 h. On the basis of final percentage weight loss and total nickel content, a model was developed to calculate the extent of reduction from TG data (see Appendix). The model predicts a 2.66% weight loss if a 10 wt% nickel catalyst is 100% reduced. Experimentally a weight loss of 2.65% was measured. Since the difference was within the uncertainty of TG and AA data, it was concluded that the catalyst was completely reduced to metallic nickel under these conditions. This is an important result for our discussion of chemisorption data later. Smith *et al.* (*17*) reported a similarly high percentage reduction (~90%) for Ni/TiO_2 catalysts, by measuring the oxygen uptake on samples reduced at 773 K.

The agreement between experimental and theoretical weight loss cited above could be fortuitous, especially in view of the fact that reduction of the support was not taken into account in the model. A series of cyclic reduction–oxidation experiments was thus performed with TG as follows:

(1) A 10 wt% Ni/Nb_2O_5 was first decomposed in nitrogen, then reduced in hydrogen at 773 K following the procedure described earlier.

(2) The reduced sample was then heated in oxygen at a linear heating rate of 10 K/min, and held at 673 K for 1 h. The purpose of this step was to determine the extent of nickel reduction as suggested by Bartholomew and Farrauto (*18*), except in this study the formation of NiO was measured gravimetrically. The oxidation was complete after 1 h, as evident from no further weight gain.

(3) Another reduction–oxidation cycle was performed on the same sample to check the reproducibility of TG data obtained in the first cycle.

TABLE 2

Weight Change Data for a 10 wt% Ni/Nb_2O_5 Sample Undergoing Reduction–Oxidation Treatment[a]

Cycle	Mass lost during reduction in H_2 (mg)	Mass gained during oxidation in O_2 (mg)
1	0.728	0.727
2	0.734	0.734

[a] Sample weight prior to the first reduction was 26.520 mg. This sample had been decomposed in flowing nitrogen to produce supported nickel oxide.

As shown in Table 2, the amount of weight loss during reduction agreed very well with the amount of weight gain during oxidation in such a series of experiments. Furthermore, the oxygen uptake at 673 K corresponded to a O/Ni stoichiometry of 1.00 ± 0.01. The excellent reproducibility and agreement of these data supported our claim that the metal was completely reduced.

It should be noted that it would be difficult to separate metal and support reduction (or oxidation) during the hydrogen (or oxygen) treatment, as the two processes most likely occur concurrently. Control TG experiments with blank Nb_2O_5 supports showed that when the oxide alone was heated in hydrogen, it started to turn blue at 673 K. However, the weight loss accompanying the reduction of the support was only about 1% of that observed during the reduction of NiO to Ni on a supported catalyst under an identical reduction treatment (773 K for 1 h). It thus appears that although some reduction of the support was necessary for SMSI, as suggested by our chemisorption results presented below, the

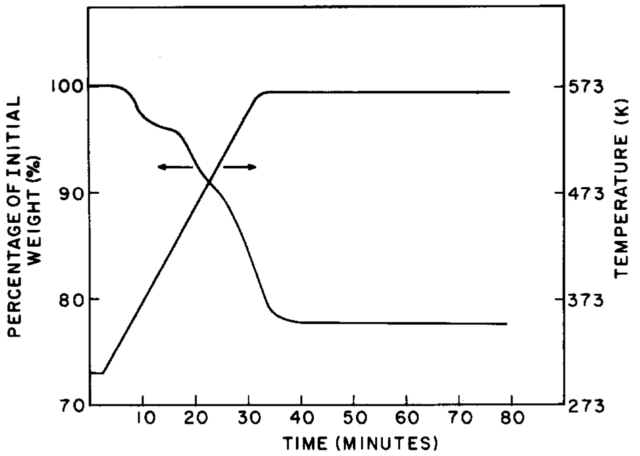

FIG. 2. The percentage weight loss and temperature versus time data as a 10 wt% Ni/Nb_2O_5 catalyst was reduced directly in hydrogen.

amount of reduction was small. The reduction of the support could thus be assumed to be negligible in our model calculations without introducing much error.

The facile reduction of Ni/Nb_2O_5 catalysts was also evident in our second reduction approach, in which the sample was directly heated in hydrogen to the reduction temperature without a preceding nitrogen treatment. It was important to examine this approach as all catalysts were directly reduced in hydrogen in the chemisorption studies. As shown in Fig. 2, the weight loss for a 10 wt% sample was already constant a few minutes into the holding period at 573 K, indicating no further reduction. Similar results were also obtained for the 2 wt% sample.

3.2. Chemisorption Behavior

3.2.1. Effect of crystallite size and reduction treatment. The chemisorption behavior of Ni/Nb_2O_5 catalysts with respect to hydrogen was studied as a function of metal loading and reduction treatment. A blank run showed that there was no hydrogen adsorption on a reduced support under our experimental conditions. The pulse chemisorption results are shown in Fig. 3, in which the cumulative hydrogen uptake was plotted against the number of injected pulses for the first 10 pulses. The uptake was expressed in terms of the ratio of number of hydrogen atoms to number of *surface* nickel atoms, rather than the number of *total* nickel atoms commonly used. The number of surface atoms was calculated from the average crystallite size as determined by X-ray diffraction. Even with the uncertainty associated with X-ray line broaden-

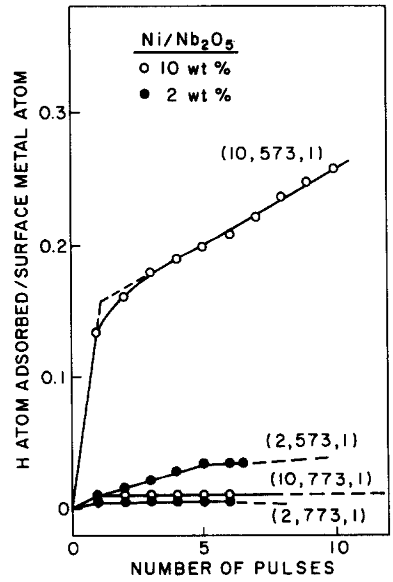

FIG. 3. Pulse chemisorption data as a function of metal loading and reduction treatment.

ing measurement, it is felt that the $H/M_{surface}$ ratio is a convenient measure for SMSI catalysts. Specifically, any departure from a normal chemisorption behavior will be immediately apparent, as the $H/M_{surface}$ ratio is near unity for Ni/SiO_2 catalysts (*19, 20*). In addition, this ratio allows a direct comparison between SMSI catalysts of different crystallite size. The notation (i,j,k) will be used throughout the rest of this paper to denote a Nb_2O_5-supported nickel catalyst, where i = metal loading in weight percent; j = reduction temperature in degrees Kelvin; k = reduction time at j K in hours.

As shown in Fig. 3, the uptake curve for a 10 wt% Ni/Nb_2O_5 catalyst (the (10,573,1) sample) did not flatten out even after 10 pulses. This was an experimental artifact of the flow chemisorption technique, which measured the irreversible rather than the total chemisorption of hydrogen (*16, 19*). In our system it was found that reversibly adsorbed hydrogen desorbed into the carrier stream during the time between two injected pulses. This desorption process occurred slowly throughout the 4-min interval such that the hydrogen coming off was below the detection threshold of the integrator. As a new pulse was injected, some of the hydrogen readsorbed onto the reversible sites resulting in an apparent uptake even though all irreversible sites had been saturated. Such an apparent uptake was corrected by drawing a straight line through the section of the uptake curve which showed a constant slope, and extending it to intersect the tangent drawn through the initial part of the uptake curve. The adsorption stoichiometry reported in this study was given by the intersection of these two lines, as shown in Fig. 3. It has been established that (*16, 19*) the dynamic pulse technique will give an adsorption stoichiometry lower than that obtained with static chemisorption due to the desorption of weakly held hydrogen. In addition, the result is known to be sensitive to operating parameters such as carrier flow rate and time between pulse injections. All measurements in this study were thus made under the same set of experimental conditions to allow a direct comparison between catalysts. For example, the results in Fig. 3 clearly show that the suppression in hydrogen chemisorption was more pronounced for the (10,733,1) than the (10,573,1) sample. On the other hand, it should be cautioned that the reported adsorption stoichiometries represent relative rather than absolute values, especially if a comparison is to be made between dynamic and static measurements.

It is clear from our earlier discussion of TG data that the low hydrogen uptake could not be due to incomplete reduction. In addition, X-ray diffraction studies on reduced catalysts showed no evidence of metal agglomeration. The chemisorption behavior of Ni/Nb_2O_5 catalysts was in fact characteristic of a SMSI system, as reported by Tauster *et al.* (*3*). Our results thus confirmed that Nb_2O_5 is an interacting support for nickel, as well as for iridium as previously shown (*14*).

It is also apparent from Fig. 3 that the (2,573,1) Ni/Nb_2O_5 catalyst had a lower $H/M_{surface}$ ratio than the (10,573,1) catalyst. As the former sample had a smaller average crystallite size, this difference suggests that the same extent of metal-support interaction would have a larger effect on the smaller crystallites. Haller *et al.* reached a similar conclusion for Rh/TiO_2 catalysts (*5*). In our laboratory the same trend has previously been observed for Ni/TiO_2 catalysts (*21*). In fact, a comparison between TiO_2- and Nb_2O_5-supported nickel catalysts shows that the suppression in hydrogen chemisorption is always more severe with Nb_2O_5 as a support, when parameters such as crystallite size and reduction treatment are held roughly constant (Table 3). These results were qualitatively similar to those obtained by Tauster and Fung (*14*) for supported Ir catalysts, and those authors suggested that the extent of interaction can be correlated with the reducibility of the sup-

TABLE 3

Chemisorption Behavior of TiO_2-[a] and Nb_2O_5[b]-Supported Nickel Catalysts

Catalyst (Average crystallite size)	No. of H atom / Surface Ni atom	
	573 K reduction (1 h)	773 K reduction (1 h)
10 wt% Ni/TiO_2 (8 nm)	0.80	0.15
10 wt% Ni/Nb_2O_5 (9 nm)	0.16	0.02

[a] Reference (*21*).
[b] This work.

port. Following their treatment, we calculated the equilibrium constants for the reduction of TiO_2 and Nb_2O_5 from literature data (*22*). As shown in Fig. 4, Nb_2O_5 is indeed more reducible than TiO_2 over a wide temperature range. It needs to be pointed out, as did Tauster and Fung (*14*), that the values in Fig. 4 correspond to bulk thermodynamic data for arbitrarily chosen reduction paths. Sexton *et al.* (*23*) recently used XPS to identify surface Nb^{2-4+} species on a Nb_2O_5 sample reduced by ion sputtering, and suggested that these reduced cations are responsible for the SMSI electron transfer. Their observation is consistent with our chemisorption results, which reinforce the important role of oxide reducibility as well as crystallite size in a SMSI system.

3.2.2. Effect of heating in an inert gas. In order to ascertain whether the different behavior between the (10,573,1) and the (10,773,1) samples was due to a further reduction of the Nb_2O_5 support, we did several experiments in which the sample was reduced at 573 K for 1 h, cooled in flowing hydrogen to room temperature, then heated *in a flowing inert gas* to 773 K, and held at that temperature for 1 h. A pulse chemisorption was run following the standard procedure after such a treatment. When nitrogen was used as an inert gas, the $H/M_{surface}$ ratio was found to be close to 0.06. This value was between those obtained for the (10,573,1) and the (10,733,1) samples. With either helium or argon as an inert gas, however, the $H/M_{surface}$ ratio dropped further to approach the value of the (10,773,1) sample.

The above observation is interesting, as it suggests a further reduction of the support even when the sample was heated in an inert environment from 573 to 773 K. To explain this observation, it is necessary to examine the reduction process more closely. The reduction of surface oxide involves the removal of oxygen through water formation (*24*). Huizinga and Prins (*12*) showed that dehydration via the removal of surface hydroxyl groups is irreversible at 773 K for a Pt/TiO_2 sample, but at 573 K some hydroxyl groups remain on the surface. Parfitt (*25*) also indicated that dehydroxylation from a TiO_2 surface is incomplete until around 773 K. Even though the dehydroxylation process may be different on different oxide surfaces, it seems plausible that heating a Ni/Nb_2O_5 catalyst in an inert gas from 573 to 773 K removed remaining hydroxyl

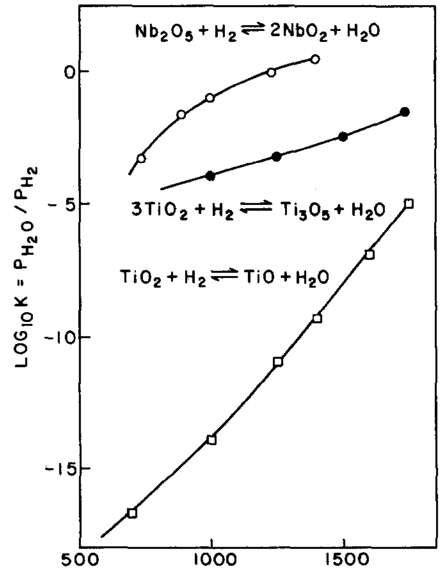

FIG. 4. Thermodynamic data for the reduction of titania and niobia.

groups from the oxide surface. This would in turn lead to more reduction of the oxide, and a further suppression in hydrogen chemisorption as observed. As for the difference between using nitrogen versus helium or argon as an inert gas, it is likely that, similar to Ni/TiO_2 catalysts (*26*), nitrogen adsorbed on the reduced Nb_2O_5 support to partially suppress the metal-support interaction.

It may be argued that the above effect was due to other factors, such as the partial oxidation of the metal surface by water from the support when the sample was heated in the inert gas. It is indeed difficult to rule out this possibility on the basis of hydrogen adsorption data alone. However, in a subsequent paper, we will present activity and selectivity data for CO hydrogenation to show that heating in an inert gas did result in a more interacting catalyst.

3.2.3. Temperature-programmed desorption study. As mentioned in the experimental section, two desorption–adsorption cycles were performed on each catalyst in this study. Regardless of what the final state of the catalyst was (i.e., whether it was a SMSI catalyst or not), the first TPD run always showed a profusion of desorbing hydrogen. The crystallite size calculated from the amount of hydrogen desorbed was in fair agreement with that determined by X-ray technique, suggesting a near monolayer coverage of hydrogen on the metal surface. As some hydrogen desorbed when the sample was purged in a carrier stream of nitrogen prior to heating, the TPD results underestimated the hydrogen coverage and gave a higher crystallite size. This effect became more pronounced with increasing purging time and carrier flow rate. The important point to note is that for a SMSI catalyst, the second TPD run showed no detectable amount of desorbing hydrogen. This unexpected observation of the difference between two TPD runs is illustrated in Fig. 5 for the (10,773,1) sample. For comparison the chemisorption behavior of a 30 wt% Ni/SiO_2 was examined by the same procedure, and the TPD spectra obtained in the two cycles were found to be reproducible (*27*).

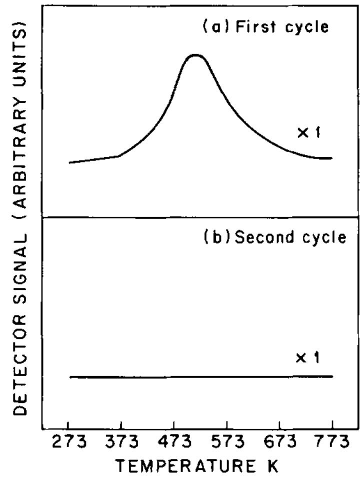

FIG. 5. Temperature programmed desorption spectra for hydrogen from a 10 wt% Ni/Nb_2O_5 catalyst: (a) first cycle, obtained after the catalyst was cooled in flowing hydrogen following reduction at 773 K; (b) second cycle, obtained after the catalyst was exposed to flowing hydrogen at room temperature for 1 h.

One possible explanation for the difference between the two TPD runs could be the activated adsorption of hydrogen due to metal-support interaction which has recently been found for cobalt catalysts on a wide variety of supports (*29, 30*). To examine this point further a sample was exposed to flowing hydrogen, after the first TPD run, at 373 K rather than room temperature for 1 h. The subsequent TPD run still showed no detectable amount of hydrogen, indicating no enhanced uptake at a higher adsorption temperature. In a separate experiment a sample was reduced following the usual procedure, but exposed to flowing nitrogen for 15 min before *switching back and cooling down in flowing hydrogen*. The first TPD run after such a treatment showed no hydrogen desorption. In contrast when a Ni/SiO_2 catalyst was subjected to the same treatment, TPD showed that it readsorbed hydrogen following nitrogen purging. On the basis of these results we speculate that the mechanism responsible for suppressing hydrogen chemisorption occurred *after* hydrogen atoms had desorbed. In other words, during reduction and cooling down of the sample in flowing hydrogen, the nickel surface remained covered with hydrogen atoms. After the first TPD run had completely desorbed hydrogen atoms, the onset of metal-support interactions rendered the metal inactive for further uptake as shown by the subsequent pulse chemisorption and the second TPD run.

4. SUMMARY

Results presented in this paper confirm that niobia is a SMSI oxide support, as shown by a suppressed hydrogen uptake on reduced Ni/Nb_2O_5 catalysts. The metal-support interaction has been found to affect the smaller crystallites more at a given reduction temperature; for a given crystallite size a higher reduction temperature results in a more severe interaction.

The correlation between oxide reducibility and the extent of metal-support interaction is further established by comparing niobia- and titania-supported nickel catalysts, and by removing surface hydroxyl groups via heating the Ni/Nb_2O_5 sample in an inert gas. On the basis of temperature-programmed desorption results, it is proposed that the interaction occurs after the desorption of surface hydrogen atoms following reduction.

In this paper the chemical characterization of Ni/Nb_2O_5 catalysts is limited to hydrogen adsorption. In a subsequent paper we shall report unique catalytic properties of these catalysts in ethane hydrogenolysis and CO hydrogenation, and show that different chemical probes identify different stages of SMSI.

APPENDIX

The following assumptions are made in the development of a model which relates the percentage weight change to the percentage reduction in our TG experiment for supported-nickel catalysts:

(i) during the nitrogen treatment the nickel salt decomposes to nickel oxide,

(ii) during the hydrogen treatment nickel oxide is reduced to a mixture of nickel oxide and metallic nickel; their relative amount gives the extent of reduction, and

(iii) both nickel oxide and metallic nickel can be dissolved in HNO_3 solution, and their concentrations determined by atomic absorption.

As mentioned earlier, assumption (i) was confirmed by X-ray diffraction. Assumption (iii) was verified by measuring the nickel concentration with atomic absorption before and after the hydrogen treatment. Assumption (ii) is the basis of the following derivation.

For 1 g of support, let y grams be the total nickel content determined by atomic absorption. Of this y grams, xy grams is in the form of nickel and $(1 - x)y$ grams is in the form of nickel oxide. The total weight of the sample after reduction, W_f, is then given by:

$$W_f = \underset{\text{support}}{1} + \underset{\text{nickel}}{xy} + \underset{\text{nickel oxide}}{(1 - x)y\left(\frac{74.71}{58.71}\right)}$$

where x is the fraction of NiO which is reduced and has a value between 0 and 1.

The initial weight before reduction, W_i, is given by

$$W_i = 1 + xy\left(\frac{74.71}{58.71}\right) + (1 - x)y\left(\frac{74.71}{58.71}\right)$$

The percentage weight change $= \dfrac{W_i - W_f}{W_i} \times 100\%$

$$= \left(\frac{16xy}{58.71 + 74.71y}\right) \times 100\%$$

This expression shows that, for a given y, the percentage weight change varies linearly with the percentage reduction. As an example, for a 10 wt% Ni/Nb_2O_5 catalyst, y would have a value of 0.111. The above expression becomes

$$\%\ \text{weight change} = 2.66x\%$$

The percentage weight change corresponding to a 100% reduction would thus be

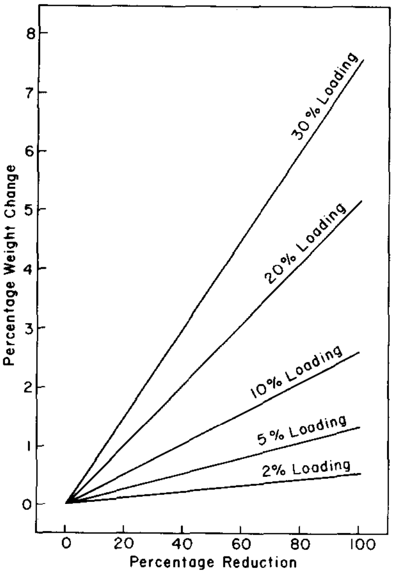

FIG. A1. Percentage reduction of supported nickel catalysts as a function of metal loading and percentage weight loss.

2.66%. Values corresponding to other metal loadings are similarly calculated and plotted in Fig. A1.

The above model does not allow for any reduction of the support itself. However, it is still applicable to a SMSI system provided the amount of oxygen lost by the support is insignificant compared to that lost by nickel oxide. The validity and implication of this assumption are discussed in Section 3.1.

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