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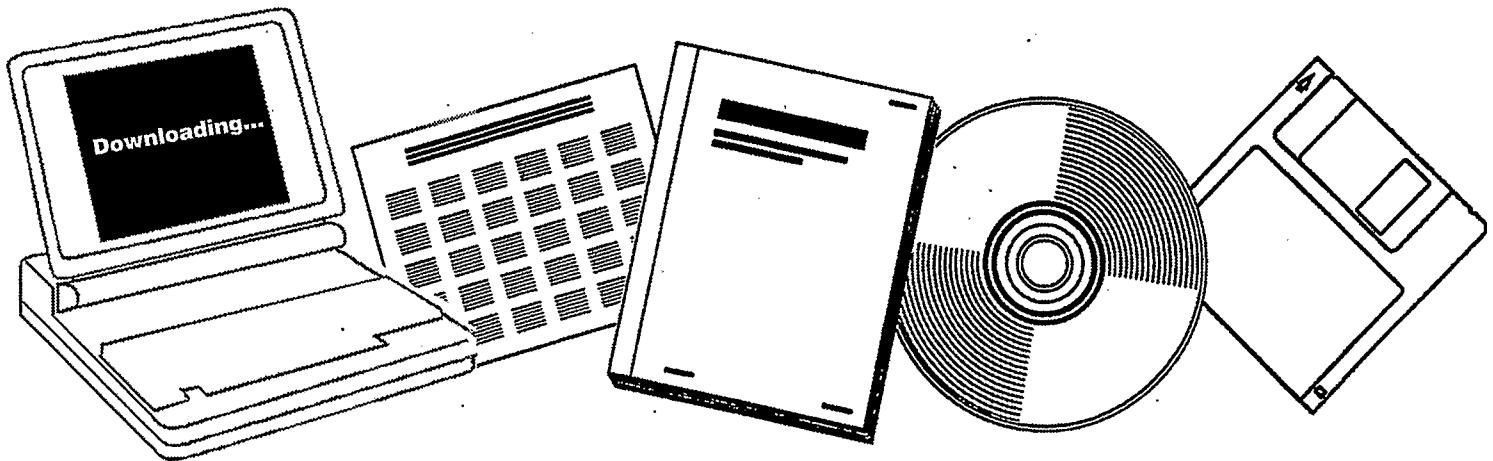
CO HYDROGENATION AND ADSORPTION STUDIES ON SUPPORTED NICKEL SMSI CATALYSTS

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CO Hydrogenation and Adsorption Studies on Supported-Nickel SMSI Catalysts

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The uptake of CO by Ni/TiO_2 and Ni/Ti_2O_3 was investigated at 25 and 125°C following low-temperature (LT = 250°C) and high-temperature (HT = 450°C) reduction. Infrared spectroscopy was used to identify the onset of nickel carbonyl ($Ni(CO)_x$) formation under various conditions of temperature and pressure. The CO uptake data were modeled using the Langmuir equation for isothermal adsorption. Monolayer coverages and equilibrium constants for CO adsorption were obtained from the uptake data. Carbon monoxide monolayer coverages were not affected by the reduction temperature of either Ni/TiO_2 or Ni/Ti_2O_3. Methanation activity at 275°C was approximately a factor of 2 greater for the Ni/TiO_2 (LT) than the Ni/TiO_2 (HT) catalyst. This correlated well with the relative strength of the CO–metal surface bond, which also decreased by a factor of approximately 2. These findings suggest that the enhanced methanation rate observed on TiO_2 supported catalysts is not due to the presence or absence of a strong metal–support interaction condition of the TiO_2 but to other properties of TiO_2 as compared to other supports. © 1985 Academic Press, Inc.

INTRODUCTION

The marked decrease in carbon monoxide and hydrogen chemisorption capacity and, in some cases, the vastly different catalytic properties of TiO_2-supported group VIII transition metal catalysts have been topics of great interest since Tauster and co-workers reported a strong metal–support interaction (SMSI) in 1978 (1). Initially, many models for the SMSI effect were put forward, but only recently has evidence been reported for the observed SMSI phenomenon on TiO_2-supported nickel (2–4).

It has been shown that TiO_x ($1 < x < 2$) species are present on supported-nickel surfaces in the SMSI state (3, 4). Raupp and Dumesic (2) have demonstrated that adsorbed TiO_x gives rise to the reduced CO coverage over a nickel foil, a phenomenon characteristic of SMSI. Kao et al. (5) have

demonstrated that extensive Ni–titania interdiffusion takes place at temperatures as low as 300°C. Taken together, these observations suggest that TiO_x migration to the surface of bulk Ni particles plays an important role in the SMSI phenomenon on Ni/TiO_2.

The studies reported here were conducted to establish the correlation, if any, between the adsorptive and the catalytic properties of nickel supported on TiO_2 and Ti_2O_3 reduced at low (250°C) and high (450°C) temperatures. Ti_2O_3 was chosen to test the importance of the bulk Ti^{3+} concentration, since reduced forms of titania are thought to play a role in the SMSI state.

EXPERIMENTAL METHODS

Materials

Catalysts were prepared by the impregnation method using reagent-grade $Ni(NO_3)_2 \cdot 6H_2O$ obtained from Fisher Scientific Company. The supports used in this work were TiO_2 (Matheson, Coleman, &

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Bell, Inc.; 75% anatase and 25% rutile; 10 m²/g), and Ti₂O₃ (Alfa Products; 5.4 m²/g). The surface area was estimated by the BET method with N₂ as the adsorbate. After impregnation, the samples were dried in air at 110–120°C for 2 hr and then calcined in air at 450°C overnight. Nickel weight loading was 10% for all catalysts.

Ultrahigh-purity hydrogen (99.999%) was further purified by passing it through a Deoxo purifier (Matheson Corp.). Carbon monoxide (99.99% purity, Matheson) was passed through a molecular sieve trap at 155°C to remove any carbonyls. Helium (99.9999% purity) flowed through an alumina trap before use.

Apparatus and Procedure

Adsorption measurements were performed in a conventional glass vacuum system capable of achieving a dynamic vacuum of 10^{-5} Torr. Pressures were measured with a MKS Baratron capacitance manometer to determine the amount of CO adsorption.

Approximately 0.3 g of catalyst was placed in a Pyrex adsorption cell and evacuated while heating to 200°C for 45 min at a pressure of less than one millitorricelli. The catalyst was then reduced in situ for 2 hr using 760 Torr hydrogen at either 250°C (LT) or 450°C (HT). During this period the H₂ was changed three times. The temperature was then lowered to 200°C while evacuating for 30 min to a pressure of less than one millitorricelli.

CO uptake studies were performed at 25 and 125°C. Fifteen to thirty min were allowed for equilibrium before each new measurement. For the 25°C study, the dual-isotherm technique (6) was used to determine the amount of strongly held CO adsorbed at different coverages. Two isotherms were measured, with a brief evacuation between them, and then subtracted to account for only the strongly held species. At 125°C, only one isotherm was measured for each catalyst since adsorption by the support

materials was insignificant and Ni(CO)₄ formation was strongly suppressed.

The procedures for IR experiments were similar to those reported in a previous paper from this laboratory (7). Infrared spectra were taken on a Nicolet 7199 FT-IR spectrometer and recorded in absorbance with 2 cm⁻¹ resolution. Absorption due to the CaF₂ windows, gas phase, and the disk background were subtracted. The catalyst disks, 20–30 mg/cm², were pressed between two pieces of paraffin paper.

CO hydrogenation was carried out in a quartz, fixed-bed reactor operating in a differential mode at low conversions. Samples of 0.2–0.4 g were pretreated in situ in flowing H₂ at either 250°C (LT) or 450°C (HT) for 2 hr. Reaction temperatures ranged from 200 to 300°C. The reactant gas composition ranged from 3:1 to 15:1 (H₂:CO) and CO pressures ranged from 0.05 to 0.25 atm; He was used to adjust the total pressure to 1 atm. Space velocities were varied from 18,000 to 54,000 hr⁻¹ to maintain differential conditions. A procedure similar to that used by Sinfelt (8) was employed to maintain catalytic activity as the total time on-stream increased. This consisted of cyclic 30-min purges in pure H₂ between 10-min H₂/CO exposures.

The details of the product analysis have been described elsewhere (9). A Varian 3700 gas chromatograph was used with two packed columns (⅛ in. o.d. stainless-steel columns of Chromosorb 106 and 20% OV-101 on Chromosorb P-AW). Product gas concentrations were determined with a Hewlett–Packard 3390A integrator by comparing the product peak areas to those for a standard mixture.

X-ray powder diffraction patterns were recorded by a General Electric Model XRD-5 diffractometer using Cu(Kα) radiation. The average Ni particle size was estimated by X-ray line broadening techniques. All the catalysts were prereduced in H₂ and then exposed to air at room temperature. The calculated average particle size for each of the four catalysts was 20 nm.
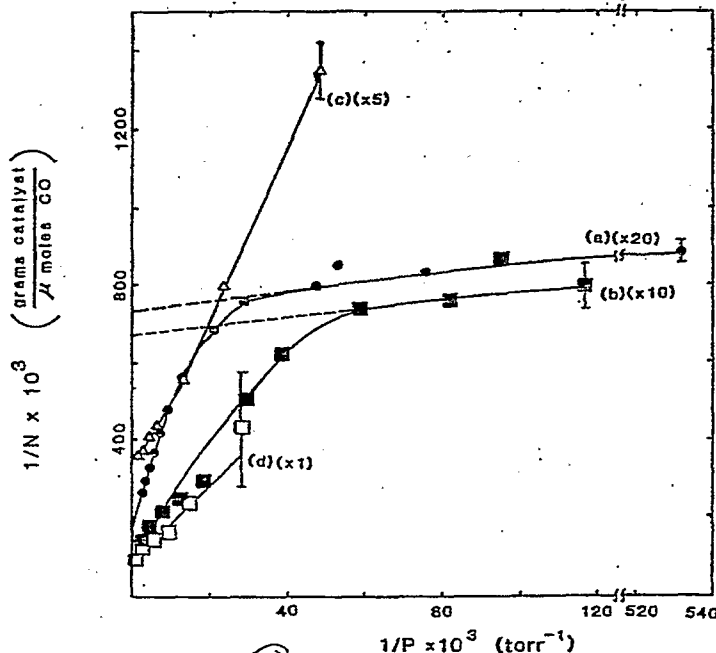
FIG. 1. Langmuir plots of the different isotherms for CO chemisorption at 25°C: (a) (●) on Ni/TiO$_2$ (LT), (b) (■) on Ni/TiO$_2$ (HT), (c) (△) on Ni/Ti$_2$O$_3$ (LT), and (d) (□) on Ni/Ti$_2$O$_3$ (HT).

RESULTS

Results at 25°C

The CO isotherms (dual and subtracted) at 25°C on 10% Ni/TiO$_2$ (LT), (HT) and 10% Ni/Ti$_2$O$_3$ (LT), (HT) catalysts are shown in Fig. 1. To make comparisons, these results were all fit using the Langmuir model for associative adsorption:

$$\frac{1}{N} = \frac{1}{N_s} + \frac{1}{N_s K_{CO}} \frac{1}{P}$$

where N = moles of CO adsorbed/g catalyst, N_s = moles of CO adsorbed/g catalyst at saturation coverage, K_{CO} = equilibrium constant for CO adsorption, and P = gas phase pressure. Values for N_s for the Ni/TiO$_2$ catalysts were determined by extrapolating the low-pressure linear section of the isotherms. The constants are listed in Table 1.

Hydrogen uptake values for each of the catalysts are presented in Table 1. Since H$_2$ adsorbs onto the surface dissociatively, sat-

uration coverage values reflect the amount of atomic hydrogen adsorbed.

Infrared spectra for CO adsorption at 25°C on Ni/TiO$_2$ (LT) and (HT) are pre-
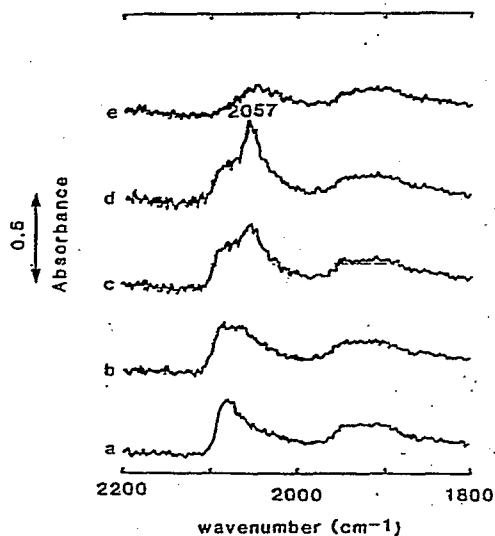

FIG. 2. IR spectra of CO chemisorption on Ni/TiO$_2$ (LT) at 25°C: (a) P_{CO} = 0.9 Torr, (b) P_{CO} = 65.9 Torr, (c) P_{CO} = 284 Torr, (d) P_{CO} = 418 Torr, and (e) evacuation at 25°C for 5 min after (d).

TABLE I

Uptake and Reaction Data

	CO uptake			H_2 uptake N_v^b (25°C)	Ni(CO)$_4$ formation P_{CO} (Torr)	Methanation	
	N_v^a (25°C)	N_s (125°C)	$K_{CO} \times 10^3$ (125°C)			E_{act} (kcal/mole)	TON $\times$ 10^3 (275°C)
10 wt% Ni/TiO$_2$ (LT)	26	26	238	78	50	33 ± 2	76
10 wt% Ni/TiO$_2$ (HT)	15	25	90	38	200	33 ± 2	35
10 wt% Ni/Ti$_2$O$_3$ (LT)	15	9.5	48	14	500	27 ± 2	14
10 wt% Ni/Ti$_2$O$_3$ (HT)	12.5	8	21	8	c	31 ± 3	22

Note. $N_v = \mu$ moles of gas adsorbed per gram of nickel catalyst at saturation coverage. TON = moles of CH$_4$ formed per second per active nickel site, based on CO uptake at 125°C.

[a] Measured using the dual-isotherm technique.

[b] Based on the adsorption of atomic hydrogen.

[c] Nickel carbonyl (Ni(CO)$_4$) was not observed to form at 125°C and P_{CO} up to 550 Torr.

sented in Figs. 2 and 3. Notice that in the Ni/TiO$_2$ (LT) study, a significant amount of the CO in the 2030–2090 cm^{-1} range (linearly bonded, subcarbonyl or carbonyl CO (*10–12*)) is removed by a brief evacuation (compare curves (d) and (e)), but that the intensity of the lower wavenumber, more strongly held bridge-bonded CO (1875–1960 cm^{-1} (*10–12*)) is undiminished. Also note the development of the distinctive nickel carbonyl band at ~2057 cm^{-1} (*12–15*) as the CO pressure is increased. This band was observed on the catalyst surface as well as in the gas phase. The IR spectra for the Ni/TiO$_2$ (HT) case (Fig. 3) also demonstrates that the species giving rise to the band at 2050–2085 cm^{-1} is removed by a brief evacuation (compare curves (b) and (c)).
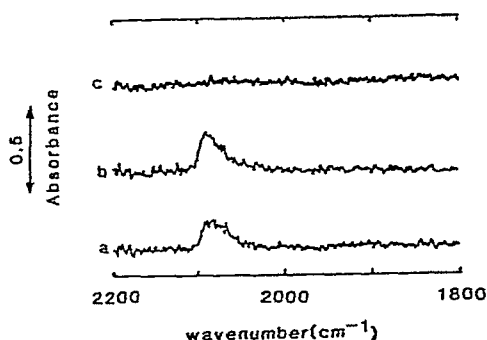
Results at 125°C

Langmuir isotherms were used to model the adsorption of CO at 125°C and are presented in Figs. 4 and 5. Uptake for pure TiO$_2$ and Ti$_2$O$_3$ at this temperature was negligible; therefore only one series of uptake measurements was performed on each catalyst. Since this procedure did not involve an evacuation step, the resultant data account for both strongly and weakly adsorbed CO. Table I includes N_s and K_{CO} values for this series of experiments.

FIG. 3. IR spectra of CO chemisorption on Ni/TiO$_2$ (HT) at 25°C: (a) P_{CO} = 0.3 Torr, (b) P_{CO} = 10 Torr, and (c) evacuation at 25°C for 5 min after exposure to P_{CO} of 368 Torr.
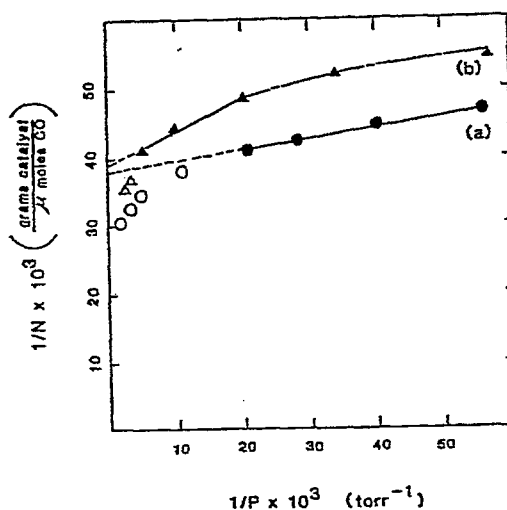
FIG. 4. Langmuir plots for CO chemisorption at 125°C: (a) (●) on Ni/TiO$_2$ (LT) and (b) (▲) on Ni/TiO$_2$ (HT). (The open symbols (O and △) correspond to uptake measurements influenced by the formation of Ni(CO)$_4$. The solid lines represent approximations to the slope of the isotherms.)
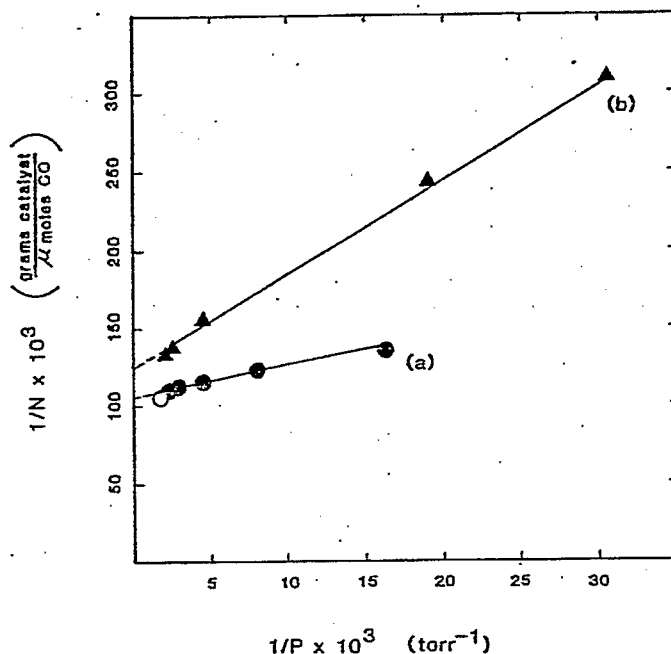
FIG. 5. Langmuir plots for CO chemisorption at 125°C: (a) (●) on Ni/Ti$_2$O$_3$ (LT) and (b) (▲) on Ni/Ti$_2$O$_3$ (HT). (The open symbol (O) corresponds to the uptake measurement influenced by the formation of Ni(CO)$_4$.)

The open symbols in Figs. 4 and 5 represent data influenced by the formation of Ni(CO)$_4$. Infrared techniques were used to verify the onset of carbonyl formation corresponding to the departures from linearity in the isotherm data. The minimum pressures at which the incipient formation of Ni(CO)$_4$ occurred on each of the catalysts are listed in Table 1.

In order to determine whether CO disproportionation or Ni(CO)$_4$ formation would be a problem if the uptake studies were performed at 125°C, an infrared study was undertaken on the Ni/TiO$_2$ (LT) catalyst. Stretching frequencies for CO$_2$ (~2330 cm^{-1}) and Ni(CO)$_4$ (2057 cm^{-1}) were not observed at 400 Torr of CO. Evidence for linear and bridge-bonded chemisorbed CO was found in the absorbances centered at 2050 and 1915 cm^{-1}, respectively.

Methanation Activity

The kinetic data for CO methanation on Ni/Ti$_2$O$_3$ (LT), (HT) are listed in Table 1.

Methanation studies were performed at 275°C using a H$_2$/CO ratio of 3 : 1. Turnover numbers (TON's) were defined as the number of moles of CH$_4$ formed per second per active Ni site for CO chemisorption at 125°C (i.e., N_s at 125°C). Activation energies for methanation were calculated from the rate data and are included in Table 1 (last two columns).

DISCUSSION

At room temperature, the tendency for Ni(CO)$_4$ to form when a supported-nickel catalyst is exposed to carbon monoxide is well documented (12, 14, 16, 17). Even though carbonyl formation on Ti$_x$O$_y$-supported nickel is somewhat suppressed in comparison to Ni/SiO$_2$ or Ni/Al$_2$O$_3$ (18), it remains a problem in obtaining accurate CO uptake data and infrared spectra of chemisorbed CO. The IR data in Fig. 2 for CO uptake at 25°C on 10% Ni/TiO$_2$ catalysts clearly indicates the formation of Ni(CO)$_4$ as CO pressure is increased. This is respon-

sible for the significant departure from linearity of the isotherms for the Ni/TiO$_2$ (LT) and (HT) catalysts (see Fig. 1), even though the dual-isotherm technique of Yates and Sinfelt (6) was used. With this method, a brief evacuation between the collection of data for the two isotherms is used to remove weakly bound species. Apparently Ni(CO$_4$) effects were not completely removed by the application of this technique and uptake results were adversely affected. In addition to influencing uptake results, Ni(CO)$_4$ formation may strip the catalyst surface of nickel and redistribute it on the infrared cell or on the catalyst itself. Thus, the formation of Ni(CO)$_4$ should be avoided if possible.

The dual-isotherm technique also assumes that only weakly held CO (mainly on the support) is removed during the evacuation step (1). However, our infrared evidence (Fig. 2) shows that a significant amount of chemisorbed CO is removed from the metal. For weakly adsorbing catalysts (as reflected by a relatively low value of K_{CO}) such as Ni/TiO$_2$ (HT) and Ni/Ti$_2$O$_3$ (LT) and (HT), a brief evacuation may remove the majority of the CO initially adsorbed on the metal. Therefore, another technique was sought that would accurately measure CO uptake and account for both the strongly and weakly chemisorbed CO.

It was with this motivation that single-isotherm adsorption studies were conducted at 125°C, a temperature at which, thermodynamically, Ni(CO)$_4$ formation is suppressed to a tolerable level and at which CO dissociation is not a problem. This was verified using IR spectroscopy. No infrared stretching frequencies for CO$_2$ (indicating CO dissociation) or Ni(CO)$_4$ were observed at 125°C and CO pressures up to 400 Torr. The onset of carbonyl formation was determined by noting deviations from linearity in the uptake isotherms (see Figs. 4 and 5). It was also determined that adsorption of CO by the pure support material was negligible at 125°C.

Using the 125°C single-isotherm uptake technique, it was possible to obtain accurate values for the equilibrium constant for CO adsorption (K_{CO}) and saturation coverage numbers (N_s) which accounted for the adsorption of both strongly and weakly held CO.

K_{CO} can be thought of as a relative measure of the average strength of CO–metal bonding; the larger K_{CO}, the more strongly the CO molecule is held to the surface. It is evident from Table 1 that there is a trend of decreasing K_{CO} as one progresses from TiO$_2$- to Ti$_2$O$_3$-based catalysts. For the TiO$_2$-supported cases, the results are in agreement with the work by Raupp and Dumesic (2), Jiang et al. (16), and Vannice and Garten (18), who found that the strength of the metal–CO bond is significantly weakened on TiO$_2$-supported catalysts in the SMSI state. This trend, however, is not reflected·in·the saturation coverage values (N_s). In fact, N_s values at 125°C for Ni/TiO$_2$ (LT) and (HT) and for Ni/Ti$_2$O$_3$ (LT) and (HT) are approximately equal. This is surprising since it has been reported that H$_2$ and CO uptake at 25°C are suppressed on Ni/TiO$_2$ (3, 16, 18, 19, 20).

In light of the above discussion we believe that significant amounts of weakly chemisorbed CO may have been overlooked. All of the procedures in question included an evacuation step which can lead to the underestimation of the amount of CO adsorbed. For example, compare N_s (25°C) to N_s (125°C) for Ni/TiO$_2$ (LT) and (HT) (Table 1). Particularly for the (HT) data, the 25°C estimates are too low because, as indicated in the IR data (Figs. 2 and 3), a significant amount of the total adsorbed CO was removed by evacuation. In the (LT) case, bridge-bonded CO (1875–1960 cm^{-1}) is not removed and the linear-bonded CO (2030–2090 cm^{-1}) is only partially removed by the evacuation step. Thus, the monolayer coverage values compare favorably. The amount of chemisorbed CO may also be underestimated in work done using high-vacuum photoelectron and Auger spectroscopies where a catalyst surface is dosed with

CO and then evacuated before any measurements are taken (see, for example, the Auger work by Takatani and Chung (3)). Our 125°C uptake studies provide no evidence for the suppression of CO uptake (i.e., N_s) on the Ti_xO_y-supported catalysts, even though K_{CO} values for the (LT) and (HT) cases differ by a factor of 2 or more.

A correlation was found between the relative value of K_{CO} for each of the catalysts and the onset of $Ni(CO)_4$ formation. As the strength of CO adsorption decreases and the overall intensity of the CO stretching frequency shifts to higher wavenumbers, the propensity for nickel carbonyl formation decreases. This is in agreement with the work of Jiang et al. (16) and Raupp and Dumesic (2).

For the titania-based systems studied here, there was no correlation between the CH_4 turnover number (TON) and either N_s or K_{CO}. However, we did find a significant decrease in the TON for Ni/TiO_2 (HT) (SMSI state) as compared to Ni/TiO_2 (LT) (non-SMSI state), in agreement with the findings of Burch and Flambard (21) and with single crystal studies by Chung et al. (4). This suggests that the enhanced methanation activity of Ni/TiO_2 over Ni/SiO_2 (TON = 3 orders of magnitude less) (21) is a characteristic of Ti_xO_y-supported metals in general and not the direct consequence of an SMSI effect. Finally, it is clear that the presence of bulk Ti^{3+} does not enhance methanation activity since the Ni/Ti_2O_3 TONs were significantly lower than those for Ni/TiO_2.

CONCLUSIONS

(1) The enhanced methanation activity of Ni/TiO_2 is not strongly correlated to the presence of an SMSI condition.

(2) The effect of (HT) reduction (SMSI) of Ni/titania catalysts is described better in terms of the strength of CO and H_2 adsorption rather than in terms of the inhibition of the chemisorption of these molecules.

(3) Techniques involving an evacuation procedure to determine the amount and/or strength of chemisorbed CO on a supported-metal catalyst surface should not be used unless it is verified that the weakly held CO, removed from the surface during the evacuation step, does not desorb from metal sites. Such a procedure will underestimate the number of active metal surface sites.

(4) Bulk Ti^{3+} does not enhance the methanation activity.

(5) Nickel carbonyl formation on the Ni/Ti_xO_y catalysts studied is inhibited as the strength of the CO–nickel surface bond decreases.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) CO uptake by Ni/TiO_2 and Ni/Ti_2O_3 was studied at 25 and 125°C following low (LT) and high temperature (HT) reduction. IR spectroscopy identified the onset of nickel carbonyl formation at various pressures and temperatures. CO uptake data were modeled using the Langmuir equation of isothermal adsorption. CO monolayer coverages were unaffected by the reduction temperature of either Ni/TiO_2 or Ni/Ti_2O_3. Methanation activity at 275°C was a factor of 2 greater for the LT than the HT Ni/TiO_2 catalyst. This correlated well with the relative strength of the CO-metal surface bond, which also decreased by a factor of 2. This suggests that the enhanced methanation rate on TiO_2 supported catalysts is not due to presence or absence of an SMSI condition, but to other properties of TiO_2 as compared to other supports.