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Metal–Support Effects on the Activity and Selectivity of Ni Catalysts in CO/H_2 Synthesis Reactions

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Titania-supported nickel catalysts exhibit unusual properties in CO–H_2 reactions relative to conventional nickel catalysts. The activity of Ni/TiO_2 is significantly greater than that of Ni powder or Ni on SiO_2, Al_2O_3, or graphite when compared on a per gram of catalyst basis or on the basis of specific activities determined from hydrogen chemisorption. In addition, the selectivity of Ni/TiO_2 relative to the other catalysts is shifted to higher molecular hydrocarbons which are paraffinic. The shift in selectivity is not accompanied by a suppression of the methanation activity, but results from an increase in the rates of chain growth reactions producing an overall increase in catalyst activity. Studies of on-stream deactivation and of the rates of $Ni(CO)_4$ formation gave further evidence of the unusual properties of Ni/TiO_2. Whereas Ni/Al_2O_3 deactivated with time on feed, Ni/TiO_2 showed little or no loss in activity, indicating a greater resistance to carbon deposition and/or metal sintering. With regard to $Ni(CO)_4$ formation, Ni/TiO_2 exhibited rates of formation at least an order of magnitude less than Ni/SiO_2 catalysts. The evidence from catalytic and chemical studies and, to a lesser extent, chemisorption and XRD investigations is indicative of a unique metal–support interaction in the Ni/TiO_2 system. The nature of the interaction which so markedly modifies catalytic and chemical properties of metals is not yet well understood.

INTRODUCTION

The role of the support in heterogeneous metal catalysts is usually considered to be physical in nature in that it provides a large surface for the formation and stabilization of small metal particles. For some time, however, there has been interest in the possibility that dispersed metals may interact with the support in such a way that the catalytic properties of the metal are significantly modified. The catalytic studies by Schwab and co-workers (*1*) on formic acid decomposition and the infrared spectroscopic investigations of CO adsorption on supported platinum by Eischens and Pliskin (*2*) some 20 years ago provided the first indications of metal–support interactions. In later work, catalytic studies of cyclopropane hydrogenation and hydrogenolysis (*3*), ethane hydrogenolysis (*4*), neopentane isomerization and hydrogenolysis (*5*), and CO–H_2 reactions (*6*) have provided further evidence that the catalytic properties of a metal depend on the support.

In the aforementioned reports, changes in kinetic parameters, i.e., specific activities and apparent activation energies, were normally cited as evidence for metal–support interactions. In contrast, Tauster

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et al. in a recent report (*7*) have provided convincing evidence, based on a dramatic modification of chemisorption properties, for a unique metal support interaction in Group VIII noble metal/TiO_2 catalysts. These materials, following reduction at 773°K, exhibited H/M and CO/M ratios near zero even though transmission electron microscopy and X-ray diffraction measurements demonstrated conclusively that the metal particles were well dispersed. Impurities or encapsulation of the metals were ruled out as possible factors leading to the conclusion that the suppression of H_2 and CO adsorption resulted from a metal–support interaction unique to the TiO_2 system.

The modification of the H_2 and CO adsorption properties of metals by the support should have significant effects on reactions between these two molecules. This follows from the recent work of Vannice (*8*, *9*) who uncovered correlations between the heats of adsorption of CO and H_2 on metals and their specific activities for methanation and total CO conversion. The correlation was further substantiated by studies of the CO–H_2 reaction over supported platinum and palladium, in which it was found that the catalyst predicted to favor the more weakly bound CO adsorbed species possessed the higher specific activity (*6*). The modification of the H_2 and CO adsorption properties reported for TiO_2 supported metals (*7*) and the correlations of Vannice (*6*, *8*, *9*) prompted the investigation of TiO_2 catalysts in CO–H_2 reactions. One system, Ni/TiO_2, was investigated in detail in this study because extensive data for nickel on a variety of other supports is available (*10*) for comparison.

EXPERIMENTAL METHODS

Materials. The TiO_2 support used in this investigation was obtained from the Cabot Corporation under the trade name Cab-O-Ti. This material was prepared by the flame hydrolysis of $TiCl_4$ and had a BET surface area of ~ 50 m^2 g^{-1}. The purity of Cab-O-Ti was reported by the manufacturer to be 99.8%, the average particle size was 0.03 μm, and the crystalline phases present were anatase (85%) and rutile (15%). Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] for the catalyst preparations was reagent grade obtained from Matheson, Coleman and Bell, Inc. The Ni/TiO_2 catalysts were prepared by the incipient wetness technique. In this method, TiO_2 is impregnated with nickel nitrate solutions of the appropriate concentrations in a ratio of 0.25 ml/g of TiO_2. The impregnates were dried in air at 110–120°C for 16 hr.

The 5% Ni/η-Al_2O_3, 8.8% Ni/η-Al_2O_3, 16.7% Ni/SiO_2 and Ni (reduced NiO powder) catalysts were all prepared in our laboratory. The preparation and properties of these catalysts have been described in detail in a previous publication (*10*). The 42% Ni/α-Al_2O_3, 31% Ni/α-Al_2O_3, and 20% Ni/graphite catalysts were commercially available samples obtained from Chemetron Corp., Catalyst Consulting Services, and Ventron Corp., respectively. The properties of these catalysts have also been described previously (*10*).

Hydrogen of 99.95% purity was obtained from the Linde Company. For chemisorption studies, the hydrogen was passed through a Deoxo unit (Engelhard Industries, Inc.), a 5A molecular sieve drying trap, an Oxy-Trap (Alltech Associates, Arlington Heights, Ill.), and finally through a liquid nitrogen trap before exposure to the catalysts. For kinetic studies, the hydrogen was passed through a Deoxo unit and a 5A molecular sieve drying trap. Carbon monoxide of 99.99% purity was obtained from the Matheson Company, and passed through a dry ice–isopropanol trap for chemisorption studies and through a molecular sieve trap in the kinetic investigations. For the superatmospheric pressure studies a 3/1 H_2–CO mixture obtained from the Matheson Company was used. The H_2–CO mixture was passed through a molecular sieve trap maintained at 353°K to decompose any metal carbonyls which may have formed in the storage cylinder. Blank H_2–CO experiments on a pure TiO_2 support at reaction conditions gave zero conversion indicating no carbonyl decomposition and metal deposition in the reactor.

Apparatus and procedure. The dihydrogen and carbon monoxide adsorption studies were conducted with a mercury-free, glass vacuum system. Ultimate dynamic vacuums of about 10^{-7} Torr (1 Torr $= 133.3$ Nm^{-2}) were obtainable using an 80 liter/sec oil diffusion pump bracketed by two liquid nitrogen traps and backed by a mechanical pump. A Texas Instruments quartz spiral Bourdon gage was used for pressure measurements.

The pretreatment conditions and procedures for chemisorption measurements on the silica, alumina, graphite, and unsupported nickel catalysts have been described in previous work (*10*). For the Ni/TiO_2 catalysts a similar procedure was adopted. Fresh or used samples were reduced in flowing hydrogen at a space velocity of 200–500 min^{-1}. Temperature was increased over a period of ~ 1.5 hr to 723°K and maintained at this temperature for 1 hr followed by a 1-hr evacuation at 698°K. Finally, the samples were cooled under dynamic vacuum to room temperature where the chemisorption measurements were determined. Longer reduction and evacuation periods for the Ni/TiO_2 catalysts did not significantly affect the adsorption results.

Dihydrogen and carbon monoxide uptakes were determined at $25 \pm 2°C$ on the reduced and evacuated samples. Typically, 30–60 min were allowed for each uptake point. The H/M ratios were calculated by assuming that no H_2 uptake occurs on the support at zero pressure of H_2. These uptakes were determined by extrapolation of the high pressure linear portion of the isotherm as described by Benson and Boudart (*11*) and Wilson and Hall (*12*). The CO/M ratios were calculated by determining the CO uptakes on the reduced and evacuated samples and assuming that this represented the sum of CO weakly bound to the support and strongly bound to the metal. The sample was then evacuated 1 min at room temperature and a second CO isotherm was measured. Since the second isotherm measures only the CO weakly adsorbed on the support, subtraction of the two isotherms gives the amount of strongly bound CO which is associated with the metal. In accordance with previous studies (*10*), the amount of strongly bound CO at 10 cm pressure was chosen as saturation coverage of the metal.

The apparatus and procedure for the kinetic studies at atmospheric pressure have been described before (*8*). Briefly, the synthesis reaction was studied with a down-flow glass tubular reactor which contained 0.1 to 0.5 g catalyst supported on a glass frit. Product distributions were determined using a Hewlett–Packard 7620 GC with Chromosorb 102 columns and subambient temperature programming. Peak areas were calculated by a Hewlett–Packard 3370 electronic integrator. Gas samples were analyzed after 20-min reaction periods which were bracketed by 20-min H_2 treatments at the reaction temperature similar to the method described by Sinfelt (*13*). This procedure prevented catalyst deactivation and gave reproducible results.

The high-pressure kinetic measurements were conducted in a 3/8-in. stainless-steel tubular reactor containing less than 0.2 g catalyst. The bracketing technique was not utilized in the high pressure studies, which were run continuously. Both the preheater and reactor sections were immersed in a fluidized sand bath. Flow rates were determined by passing the exit gas from the reactor through a bubble meter and a wet test meter. Errors introduced by the technique were small provided CO conversions were low (~5% or less). These measurements, however, were less accurate than those routinely determined on the atmospheric test unit.

Catalyst pretreatments prior to the kinetic studies for the silica, alumina, graphite, and unsupported nickel catalysts have been described previously (*10*). For the Ni/TiO_2 catalysts, samples were heated to 723°K in hydrogen at a space velocity of ~200 min^{-1} over a period of approximately 1.5 hr. The samples were reduced for 1 hr at 723°K and then cooled in hydrogen to the reaction temperature.

A Phillips Electronics X-ray diffractometer (XRG-300) with nickel-filtered Cu $K\alpha$ radiation was used for X-ray diffraction studies of the catalyst samples. Nickel crystallite sizes were calculated from X-ray line broadening measurements as described elsewhere (*14*).

RESULTS AND DISCUSSION

Characterization of Catalysts

Chemisorption and X-ray diffraction studies were utilized to characterize the nickel catalysts. The results of the chemisorption studies on fresh and used catalysts are summarized in Table 1. The results for the Al_2O_3, SiO_2, graphite, and unsupported nickel catalysts have been discussed in earlier work (*10*) and are included here for comparison to the Ni/TiO_2 samples.

The primary question which we shall consider for the Ni/TiO_2 samples is whether or not there is evidence from adsorption and X-ray studies of a metal–support interaction of the type described by Tauster *et al.* (*7*) for Group VIII noble metal/TiO_2 samples. Tauster *et al.* demonstrated that Group VIII metal/TiO_2 catalysts exhibited high values of percentage metal exposed and normal H_2 and CO uptakes following reduction at 473°K. However, when the same catalysts were reduced at 773°K, H_2 and CO uptakes dropped markedly without concomitant sintering of the metal particles as shown by X-ray diffraction and TEM. For palladium on TiO_2, the effect was completely reversible by oxidation of the sample at 673°K. Thus, a Pd/TiO_2 catalyst which exhibited very low H_2 and CO uptakes following reduction at 773°K regained the capacity for H_2 and CO adsorption fol-

TABLE 1

Characterization of Ni Catalysts by H_2 and CO Chemisorption

Catalyst	Fresh catalysts[a]		Used catalysts[a]	
	H/Ni[b]	CO/Ni[c]	H/Ni[b]	CO/Ni[c]
1.5% Ni/TiO_2	0.032	0.15	0.014	0.21
10% Ni/TiO_2	0.056	0.076	0.036	0.11
5% $Ni/\eta\text{-}Al_2O_3$	0.27	0.28	0.12	0.14
8.8% $Ni/\eta\text{-}Al_2O_3$	0.30	—	0.025	0.14
30% $Ni/\alpha\text{-}Al_2O_3$	0.13	0.099	0.12	0.12
42% $Ni/\alpha\text{-}Al_2O_3$	0.034	0.050	0.018	0.029
16.7% Ni/SiO_2	0.27	—	0.085	0.16
20% Ni/graphite[d]	0.022	0.003	0.012	0.007
NiO (reduced)[e]	0.0021	0.0031	0.0035	0.0015

[a] Samples reduced at 723°K; H_2 and CO isotherms determined at 25 ± 2°C except where noted.

[b] Ni dispersion as defined by the ratio of total Ni atoms to adsorbed H atoms.

[c] Ni dispersion as defined by the ratio of total Ni atoms to adsorbed CO molecules.

[d] Uptakes determined at 473°K.

[e] Reduced at 573°K.

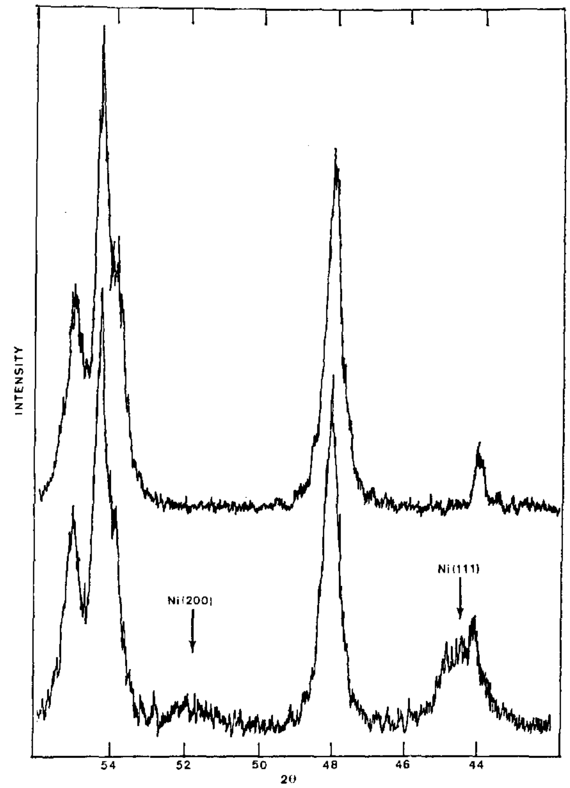

FIG. 1. X-Ray diffraction patterns for TiO_2 (upper trace) and 10% Ni/TiO_2 (lower trace) following reduction at 773°K.

lowing oxidation at 673°K and reduction at 473°K.

With supported nickel catalysts, reduction cannot be accomplished at temperatures as low as 200°C. Thus, some of the criteria used by Tauster *et al.* to detect metal–support interactions in Group VIII noble metal/TiO_2 catalysts are not applicable to nickel catalysts. As shown in Table 1, the H/Ni and CO/Ni ratios for fresh Ni/TiO_2 reduced at 723°K are similar to those observed by Tauster *et al.* for the noble metals. However, other supported nickel catalysts also show low H_2 and CO uptakes. A comparison of fresh catalyst chemisorption results for 10% Ni/TiO_2 with other catalysts of similar concentrations (5% Ni/η-Al_2O_3, 8.8% Ni/η-Al_2O_3, 16.7% Ni/SiO_2) shows Ni/TiO_2 to have much lower H/Ni and CO/Ni ratios. The BET surface area of TiO_2 is five to six times lower than that of the other supports, however, so that larger nickel particles might be expected from the TiO_2 samples.

X-Ray diffraction measurements on the Ni/TiO_2 samples provided some indication for a metal–support interaction although the evidence was not conclusive. For the 1.53% Ni/TiO_2 catalysts reduced at 723°K, XRD showed peaks due only to the anatase and rutile forms of TiO_2. The absence of Ni or NiO peaks in this instance may be due to the low Ni loading. For 10% Ni/TiO_2, XRD of the 723°K-reduced sample showed broad peaks due to Ni metal (Fig. 1). Estimation of the nickel particle size by X-ray line broadening on the nickel peaks at 2θ of 51.9° gave a value of ~7.5 nm corresponding to ~15% nickel exposed. Using the surface-to-volume relationship, $1 = 6/sd$ for particle size and assuming a value of 0.065 nm^2 for the area of a nickel atom, particle sizes of 18 and 13 nm are calculated from H_2 and CO adsorption on the fresh catalyst.

The comparison of XRD and chemisorption results suggests that chemisorption is suppressed because adsorption results are indicative of a larger particle size than is determined from XRD. Thus, although directionally the behavior of the Ni/TiO_2 system is similar to that reported by Tauster *et al.*, the evidence from the available characterization studies is much less gratifying. Careful electron microscopy studies of the Ni/TiO_2 catalyst in conjunction with chemisorption measurements are necessary to decide whether the average nickel particle size is much less than that indicated by chemisorption and, therefore, indicative of metal-support interaction.

Although the available characterization studies did not provide convincing evidence for metal-support interaction in the Ni/TiO_2 system, studies of the activity and selectivity of these catalysts gave evidence of such an interaction. These studies are discussed in the following sections.

Activities

The activities of the nickel catalysts were evaluated under differential reaction conditions using finely divided catalyst powders to eliminate heat and mass transfer effects. Calculations using the Weisz criteria (*15*) and tests at two different temperatures using the Koros-Nowak criteria (*16*) as described by Madon (*17*) demonstrated the absence of heat and mass transfer limitations in the activity evaluations.

Before discussing the specific activities of Ni/TiO_2, it is informative to compare the activities of all the catalysts on a per gram nickel and per gram catalyst basis. For catalysts of comparable densities, such as the TiO_2 and Al_2O_3 samples, these comparisons directly quantify the total activity that can be achieved for a given reactor volume and are, therefore, of more practical interest. The comparisons are shown in Table 2. On these bases, the Ni/TiO_2 catalysts are the most active materials with 10% Ni/TiO_2 exhibiting 1-2 orders of magnitude greater activity than unsupported nickel or nickel on the other supports. On a per gram nickel basis, 1.53% Ni/TiO_2 is also a very active material, with its activity per gram of catalyst comparable to other catalysts with metal concentrations nearly an order of magnitude greater. The data in Table 2 show that, for practical applications, much higher reaction rates per unit reactor volume could be achieved with Ni/TiO_2 relative to the other catalysts.

TABLE 2

CO Conversion Activity of Ni/TiO_2 Relative to Other Ni Catalysts for the CO-H_2 Reaction[a]

Catalyst	moles CO converted/sec/g Ni	moles CO converted/sec/g catalyst
1.53% Ni/TiO_2	8.35	0.11
10% Ni/TiO_2	22.8	2.28
5% $Ni/\eta-Al_2O_3$	3.44	0.17
8.8% $Ni/\eta-Al_2O_3$	1.63	0.14
42% $Ni/\alpha-Al_2O_3$	0.21	0.09
16.7% Ni/SiO_2	2.36	0.39
20% Ni/graphite	0.064	0.013
Ni powder	0.032	0.032

[a] Reaction conditions: 478°K (205°C), 103 kPa (1 atm), $H_2/CO = 3$.

The determination of the specific activities of the Ni/TiO_2 catalysts is not straightforward. This is due to the possible suppression of hydrogen and carbon monoxide chemisorption because of metal-support interaction. Chemisorption measurements, therefore, may not provide a proper measure of the particle size and the active nickel sites for catalytic reaction. The gross activities in Table 2 imply that either the specific activity of Ni/TiO_2 is significantly greater than that of the other nickel catalysts or that the number of active sites for CO conversion is much larger, i.e., the average particle size for Ni/TiO_2 is much less than that of the other catalysts. The characterization studies by XRD on 10% Ni/TiO_2, however, clearly gave evidence of large nickel crystallites. It appears unlikely, therefore, that the particle size of the Ni/TiO_2 catalysts differs sufficiently from that of the other samples to account for the activity differences in Table 2. We are thus led to the conclusion that the specific activity of Ni/TiO_2 is greater than for nickel on the other supports.

Additional support for this conclusion is obtained by comparing the specific activities of Ni/TiO_2, calculated in two ways, with those of the other catalysts. Specific activities were calculated using hydrogen adsorption data and also with the *assumption* of 100% nickel exposed in Ni/TiO_2. These two calculations thus established the *upper and lower limits* on the specific activity of Ni/TiO_2. Specific activities from hydrogen chemisorption were calculated from adsorption data on the fresh and used catalysts in accordance with earlier work on nickel (*10*). These specific activities were, in general, within a factor of two.

The specific activities for CO conversion, N_{CO}, and methanation, N_{CH_4}, calculated by the procedures just described, are tabulated in Table 3. It is clear from the table that if specific activities are calculated on the basis of hydrogen chemisorption, the Ni/TiO_2 catalysts are 1–2 orders of magnitude higher in specific activities for CO conversion or methanation than the other nickel catalysts. Even with the assumption of 100% nickel exposed, which is unrealistic for 10% Ni/TiO_2 based on the XRD results, the specific activities of both Ni/TiO_2 catalysts are comparable to or greater than those for the other catalysts. The results in Table 3, therefore, are indicative of a metal–support interaction which *increases* the specific activity of nickel when TiO_2 is the support. The results in Table 3 cannot be attributed purely to particle size effects since earlier studies by Vannice (*10*) indicated that such effects can account for at most a factor of 2 in activity.

Selectivities

Table 4 compares the selectivities of the various nickel catalysts at atmospheric

TABLE 3

Specific Activities of Ni/TiO_2 Relative to Other Ni Catalysts for the CO–H_2 Reaction[a]

Catalyst	N_{CO} ($sec^{-1} \times 10^3$)		N_{CH_4} ($sec^{-1} \times 10^3$)	
	H_2 (fresh)	H_2 (used)	H_2 (fresh)	H_2 (used)
1.5% Ni/TiO_2	500	1142	231	528
1.5% Ni/TiO_2 (100)[b]	16		7.4	
10% Ni/TiO_2	1607	2500	196	305
10% Ni/TiO_2 (100)[b]	90		11	
5% Ni/η–Al_2O_3	19.6	44	16.4	37
8.8% Ni/η–Al_2O_3	10.7	128	7	85
42% Ni/α–Al_2O_3	58	109	23.8	43
30% Ni/α–Al_2O_3	32.3	35	16.6	18
16.7% Ni/SiO_2	14.8	47	10.7	34
20% Ni/graphite	43.1	79	27.8	51
Ni powder	30	18	26.6	16

[a] Reaction conditions: 548°K (275°C), 103 kPa (1 atm), $H_2/CO = 3$.

[b] Calculated assuming 100% nickel metal exposed.

TABLE 4

Comparison of the Selectivity of Ni/TiO_2 to Other Ni Catalysts for the CO–H_2 Reaction

Catalyst	Reaction T (°K)	CO conversion (%)	mole% paraffin of each carbon number				
			C_1	C_2	C_3	C_4	C_{5+}
1.5% Ni/TiO_2	524	13.3	58	14	12	8	7
10% Ni/TiO_2	516	24	50	9	25	8	9
5% $Ni/\eta\text{-}Al_2O_3$	527	10.8	90	7	3	1	—
8.8% $Ni/\eta\text{-}Al_2O_3$	503	3.1	81	14	3	2	—
42% $Ni/\alpha\text{-}Al_2O_3$	509	2.1	76	1	5	3	1
16.7% Ni/SiO_2	493	3.3	92	5	3	1	—
20% Ni/graphite	507	24.8	87	7	4	1	—
Ni powder	525	7.9	94	6	—	—	—

pressure. Both Ni/TiO_2 catalysts exhibited a shift in product distribution to heavier hydrocarbons relative to the other nickel catalysts. Gas chromatographic analysis of the C_{2+}-hydrocarbons showed that they were predominantly *normal paraffins*. On a mole percent basis, Ni/TiO_2 makes about one-half as much methane as nickel on conventional supports. The marked shift in selectivity for Ni/TiO_2 is even more apparent when the product distribution is presented on a weight basis, which is a better representation of CO utilization and is more useful for practical considerations. This is shown in Fig. 2. On a weight basis, the product distribution is rather flat and less than one-fourth of the product weight is composed of methane. Conversion level had no significant effect on the selectivity differences between Ni/TiO_2 and the other catalysts. This is illustrated in Fig. 3 which was obtained

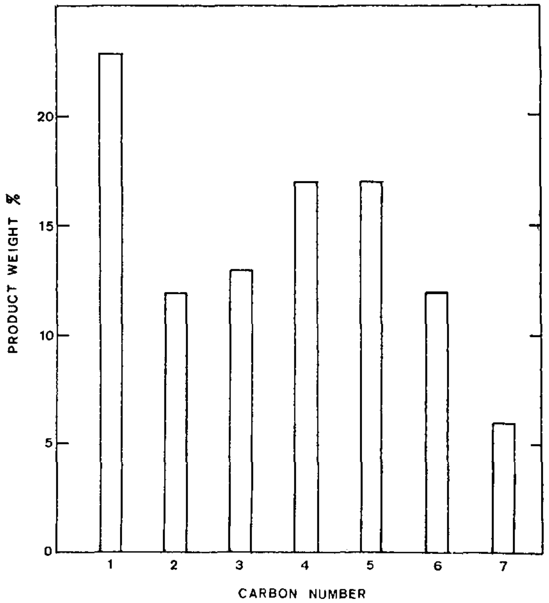

FIG. 2. Product distribution (wt%) for the H_2-CO reaction over 10% Ni/TiO_2. Data were taken at 473°K, $H_2/CO = 3$, P (total) = 103 kPa (1 atm), and 4.6% CO conversion.

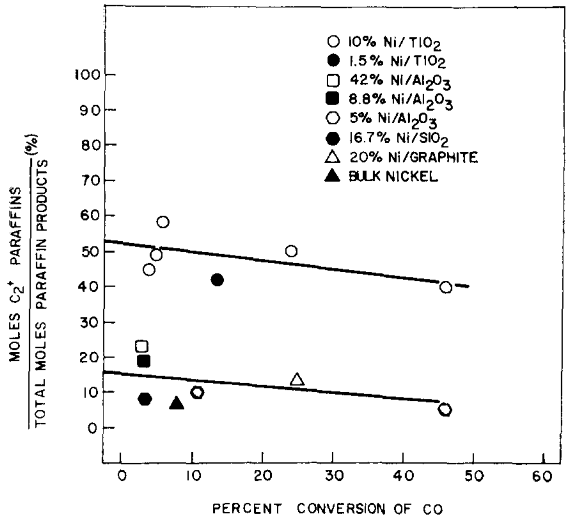

FIG. 3. Comparison of the selectivities of nickel catalysts to C_{2+}-hydrocarbons as a function of CO conversion.

by variation of the space velocity and pertains to reaction temperatures varying from 503°K (8.8% Ni/η-Al_2O_3) to 527°K (5% Ni/η-Al_2O_3). For CO conversions up to about 50%, the high selectivity to heavier paraffinic hydrocarbons was maintained for the TiO_2 catalysts. The slight decrease in selectivity with increasing conversion level may result in part from secondary hydrogenolysis reactions caused by the larger amounts of heat generated from the exothermic CO–H_2 reaction, or from an increasing H_2/CO ratio.

The effect of total reaction pressure on the selectivity and conversion at constant space velocity for 10% Ni/TiO_2 is compared to 30% Ni/α-Al_2O_3 in Table 5. Increase in total pressure tends to shift the product distribution slightly toward methane with Ni/TiO_2, but has the opposite effect on Ni/α-Al_2O_3.

It is interesting to examine the nature of the selectivity shift toward higher hydrocarbons for Ni/TiO_2. The specific activity comparisons in Table 3 showed that the turnover frequency for methanation

TABLE 5

Effect of Pressure on the Selectivity of Ni Catalysts[a]

Catalyst	Pressure (kPA (atm))	CO conversion (%)	mole% product at each carbon number				
			C_1	C_2	C_3	C_4	C_{5+}
10% Ni/TiO_2	103 (1)	4	50.5	21.5	7.5	7.5	12
	1030 (10)	3.5	56	37	5.5	1.5	—
	2060 (20)	4.5	57.5	35	5.5	2	—
30% Ni/α-Al_2O_3	103 (1)	2.1	80	16	4	—	—
	1030 (10)	1.9	69	29	2	—	—
	2060 (20)	1.3	69	31	—	—	—

[a] Reaction conditions: 476°K (203°C), H_2/CO = 3.

over Ni/TiO_2 was comparable to or greater than those of the other catalysts. Turnover frequencies for total CO conversion, however, were higher for TiO_2, particularly 10% Ni/TiO_2 on any comparison basis, than any of the other samples. The selectivity shift for Ni/TiO_2, therefore, arises from an increase in the rate of the carbon–carbon bond-making reaction without significantly affecting the methanation activity. This behavior contrasts markedly with the effect of sulfur on the selectivity of conventional nickel catalysts. The addition of sulfur to such catalysts also produces a shift in selectivity toward higher molecular weight products, but, at the same time, suppresses total activity by several orders of magnitude (*18*). Methanation activity is generally decreased drastically, whereas activity for higher molecular weight hydrocarbon formation is reduced to a much lesser extent and, in some instances, even increased (*18*). The selectivity shift to higher carbon numbers which occurs concomitantly with an increase in the total activity of the catalyst appears to be unique to the Ni/TiO_2 system, and is further evidence of an influence of the support on the chemical properties of nickel.

Deactivation of Nickel Catalysts

The deactivation characteristics of Ni/TiO_2 catalysts also differed substantially from that of Ni/Al_2O_3 catalysts. This is illustrated in Figs. 4 and 5. The experiments depicted in the figures were carried out in continuous runs on each catalyst in an increasing pressure sequence. The open symbols at each pressure represent initial data, while the filled symbols represent data after 20–30 min at the indicated pressure. For the 30% Ni/Al_2O_3, Fig. 4 shows that significant deactivation occurs at each pressure with time on feed. Furthermore, the decrease in activity at pressures above ~10 atm is undoubtedly associated with deactivation since the *total* pressure dependence of the methanation reaction over nickel is positive (*10*).

In contrast to Ni/Al_2O_3, the Ni/TiO_2 catalyst gave little evidence of any deactivation during the pressure dependence studies (Fig. 5). Deactivation at each pressure was minimal and the total pressure dependence of the methanation rate up to ~20 atm was close to the value of 0.5 determined at subatmospheric pressure by independent measurements.

The major sources of catalyst deactiva-

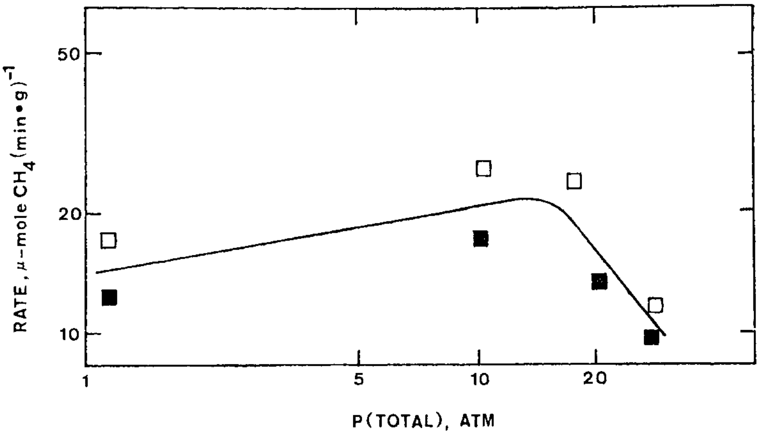

FIG. 4. Deactivation behavior of 30% Ni/Al_2O_3 at various pressures for the H_2–CO reaction. The open symbols represent initial data at each pressure whereas the filled symbols represent data after 20–30 min at the indicated pressure. Data were accumulated in a continuous run with increasing pressure at 473°K, H_2/CO = 3, and GHSV = 19,500.

tion in the pressure-dependence studies depicted in Figs. 4 and 5 were undoubtedly carbon deposition and sintering of the nickel. Unfortunately, no characterization studies were made of the spent catalysts from these studies. It may be noted, however, that the 30% Ni/Al_2O_3 exhibited no decrease in metal surface area, as determined by hydrogen adsorption, in atmospheric pressure catalytic studies (Table 1). Deactivation in this system may, therefore, arise for the most part from carbon deposition. If this is the case, the results of Figs. 4 and 5 suggest that Ni/TiO_2 is more resistant to carbidization than conventional nickel catalysts. Regardless of which deactivation mechanism is operative with Ni/Al_2O_3, it appears that Ni/TiO_2 resists it and exhibits improved stability.

Nickel Carbonyl Formation

Additional evidence of metal–support interaction in the Ni/TiO_2 system was obtained from studies of rates of $Ni(CO)_4$ formation. Samples of 10% Ni/TiO_2 and 10% Ni/SiO_2 weighing 27–29 mg were pressed into thin wafers and placed in an infrared cell identical to that described by Yates *et al.* (*19*). The samples were reduced in dihydrogen for 1 hr and then evacuated for 10 min at 500°C. Following cooling to room temperature, carbon monoxide was admitted to the samples, which were kept out of the infrared beam, and the formation of $Ni(CO)_4$ in the gas phase monitored by infrared spectroscopy. Figure 6 shows the relative rates of $Ni(CO)_4$ formation over the two samples. Clearly, the formation of $Ni(CO)_4$ is severely inhibited when TiO_2 is the support. Approximately 1 hr after CO addition, the concentration of $Ni(CO)_4$ in the gas phase over Ni/TiO_2 is more than an order of magnitude less than that over Ni/SiO_2. This aspect of the Ni/TiO_2 system is particularly attractive from a practical viewpoint because of the hazards associated with poisonous $Ni(CO)_4$.

SUMMARY AND CONCLUSIONS

This investigation provides convincing evidence for a novel metal–support interaction in titania-supported nickel catalysts. Such evidence is provided by comparisons of the activities, selectivities, and deactivation characteristics of Ni/TiO_2 relative to a variety of other nickel catalysts in $CO–H_2$ reactions, of the rates at which $Ni(CO)_4$ is formed in the presence of CO and to a lesser extent by chemisorption and XRD characterization studies.

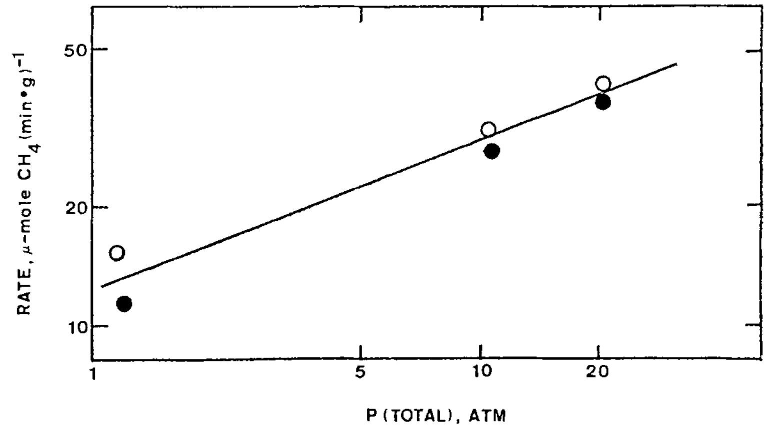

FIG. 5. Activity maintenance of 10% Ni/TiO_2 at various pressures for the H_2–CO reaction. Data were accumulated as described in Fig. 4 at 473°K, H_2/CO = 3, and GHSV = 12,000.

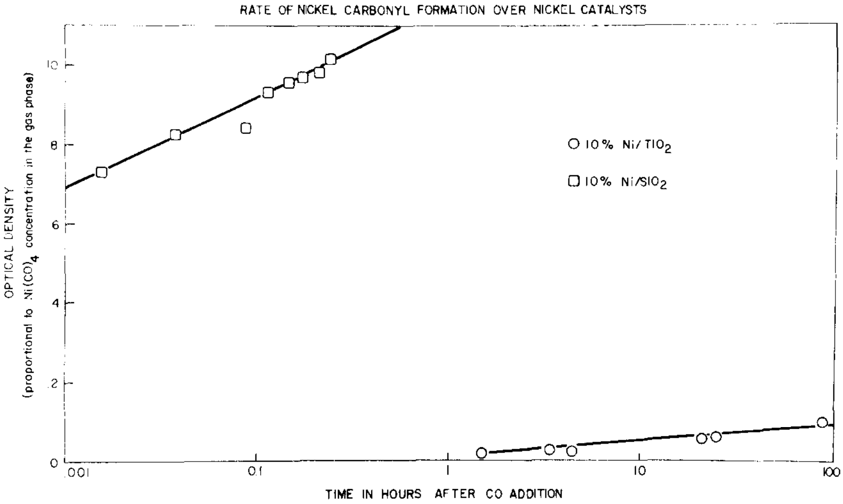

FIG. 6. Relative rates of $Ni(CO)_4$ formation for Ni/SiO_2 and Ni/TiO_2 catalysts.

The activity of Ni/TiO_2 catalysts for CO conversion is significantly greater than that of unsupported nickel or nickel on silica, alumina, or graphite. Accompanying the activity enhancement is a shift in the product distribution to higher molecular weight paraffinic products. The shift in product distribution results from an increase in the activity of carbon–carbon bond-making reactions rather than a suppression of methanation activity. This is in marked contrast to the experience with other nickel catalysts where shifts in product distribution to higher carbon numbers can be brought about by sulfur addition but at a sacrifice in activity of several orders of magnitude.

Other unique characteristics of Ni/TiO_2 were resistance to deactivation and $Ni(CO)_4$ formation. Whereas Ni/Al_2O_3 deactivated with time on feed, Ni/TiO_2 showed little evidence of any loss of activity. This suggests that Ni/TiO_2 catalysts may be more resistant to the common modes of deactivation of nickel catalysts, namely, carbon deposition and sintering. With regard to $Ni(CO)_4$ formation, the rate was decreased by more than an order of magnitude for Ni/TiO_2 relative to Ni/SiO_2.

The nature of the metal–support interaction in titania-supported catalysts remains obscure. This study shows clearly the significance and potential impact of such interactions on catalytic and chemical properties. As further studies of the physical and chemical properties of these materials are obtained from detailed characterization by analytical tools, much needed insight into the origins of the interaction may be anticipated.

In addition to providing evidence of a unique metal–support interaction in the Ni/TiO_2 system, the results of this investigation are also of significance from the viewpoint of practical applications of these materials. Recently there has been much interest in processing alternatives for the on-site production of peak-shaving fuels in coal gasification–electric power generation facilities. Two alternatives frequently considered are methanol synthesis and Fischer–Tropsch synthesis. Methanol synthesis is attractive since the product is a clean, storable liquid, but the process operates at high pressures and is costly. Fischer–Tropsch synthesis operates at lower pressures, but the product distributions from typical iron-based catalysts are complex mixtures which degrade in storage. The product distribution obtained with

Ni/TiO_2, however, is paraffinic and probably stable to storage. Also, a process utilizing Ni/TiO_2 could operate at or near atmospheric pressure, and it could be an attractive alternative to methanol or conventional Fischer–Tropsch processes for the production of peak-shaving liquids.

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