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CO Hydrogenation Reactions over Titania-Supported Nickel

In a recent paper we reported the unusual catalytic behavior of titania-supported nickel in the CO hydrogenation reaction (*1*). The two outstanding features of this catalyst, relative to conventional supported nickel catalysts, were a much higher specific activity and a shift in selectivity toward the production of higher molecular weight paraffins. Because the behavior of Ni/TiO_2 was distinctly different from typical nickel methanation catalysts, further studies were conducted to better define the alteration of catalytic properties which was attributed to metal–support interaction. In addition to measuring kinetic parameters for methanation and total CO conversion, the reproducibility of the unusual catalytic behavior using a different titania produced by Degussa was determined. The Cab-O-Ti, used in earlier work, is no longer commercially available; therefore it was important to determine if a readily available material exhibited properties similar to Cab-O-Ti.

The TiO_2 supports used in this study were obtained from two sources: Cab-O-Ti (COT) from Cabot Corporation and P-25 titania from the Degussa Company. Both samples were prepared by the flame hydrolysis of $TiCl_4$ and have very similar physical properties which have been tabulated elsewhere (*2*). The Ni/TiO_2 catalysts were prepared by the incipient wetness technique using reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ obtained from Matheson, Coleman, and Bell, Inc. (*1*). After impregnation, the samples were dried in air for 16 hr at 110–120°C. The gases used and the purification steps employed have been described previously (*1*). One additional gas mixture with a H_2/CO ratio of 1, premixed and analyzed by the Matheson Company, was used in this study. To remove any carbonyls which may have been present, this mixture was passed through a molecular sieve trap heated at 80°C before it entered the stainless-steel reactor. Details of the adsorption apparatus, pretreatment procedure, and reactor systems have been given previously (*1, 3*).

Chemisorption measurements were conducted on samples of 1.5% Ni/P-25 and 10% Ni/P-25 catalysts which had been used for reactor studies. On the former catalyst, ratios of $CO/Ni = 0.32$ and $H/Ni = 0.094$ were obtained, and on the latter catalyst ratios of $CO/Ni = 0.15$ and $H/Ni = 0.079$ were measured. As reported for the Ni/COT catalysts (*1*), CO uptakes are noticeably larger than H_2 uptakes. In the absence of carbonyl formation, typical nickel catalysts usually exhibit $CO_{(ad)}/H_{(ad)}$ ratios near unity (*4*): however, titania inhibits carbonyl formation (*1*); thus the high ratios observed for the titania-supported nickel catalysts do not seem to be attributable to this factor. Calculated average crystallite sizes based on CO or H_2 uptakes were significantly smaller than those determined from diffraction measurements indicative of a suppression of H_2 and CO chemisorption as a result of metal–support interaction (*1*).

Turnover frequencies and activation energies for the methanation reaction and for total CO conversion to hydrocarbons are given in Table 1. Over the 1.5% Ni/COT catalyst, the partial pressure dependencies on hydrogen and CO were 0.85 ± 0.10 and -0.33 ± 0.06, respectively. These values agree closely with those determined for a 5% Ni/Al_2O_3 catalyst (*3*). The inhibition of H_2 chemisorption with titania-supported metals presents a problem for the determination of turnover frequencies. As discussed in earlier work (*1*), this difficulty was addressed by determining the possible range of specific activities by calculating maximum turnover frequencies on the basis

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TABLE 1

Kinetic Behavior of Titania-Supported Nickel[a]

Catalyst	Turnover frequency						Activation energy	
	N_{CH_4} ($sec^{-1} \times 10^3$)			N_{CO} ($sec^{-1} \times 10^3$)			E_{CH_4} kJ mole^{-1}	E_{CO} kJ mole^{-1}
	b		*c*	*b*		*c*		
1.5% Ni/COT	231		528	500		1140	115	111
1.5% Ni/COT[d]		7.4			16			
10% Ni/COT	196		305	1610		2500	114	132
10% Ni/COT[d]		11			90			
1.5% Ni/P-25	—		140	—		430	113	116
1.5% Ni/P-25[d]		13			41			
10% Ni/P-25	—		180	—		630	136	116
10% Ni/P-25[d]		14			50			

[a] $P = 101$ kPa, $H_2/CO = 3$, $T = 275°C$.

[b] Based on H_2 chemisorption on fresh catalyst.

[c] Based on H_2 chemisorption on used catalyst.

[d] Based on the assumption of a fraction exposed = 1.

of H_2 chemisorption to count metal sites, while minimum values were calculated by assuming a fraction exposed equal to 1. The latter is clearly an overestimate of nickel surface area with 10% Ni/TiO_2 for which the X-ray diffraction pattern showed reflections due to nickel crystallites. All calculated turnover frequencies are shown in Table 1. Even the minimum estimates for N_{CO} values over Ni/COT are comparable to or greater than those measured on typical nickel catalysts (*1*).

Curtailment of the commercial production of Cab-O-Ti led to the use of P-25 titania available from Degussa. Although some variations were found, the higher activity and enhanced formation of longer-chain *n*-paraffins obtained with COT titania were reproducible using P-25 titania (Tables 1 and 2). In fact, the enhanced production of higher molecular weight paraffins reported earlier for 10% Ni/COT (*1*) was even more pronounced with 10% Ni/P-25, as shown in Table 2. Under identical conditions, methane formation was suppressed to 15 wt% in some cases and C_8 hydrocarbons were easily detectable. Figure 1 shows the product weight fractions for three different runs, with two runs on 10% Ni/COT indicating the influence of temperature on the product distribution. When the reaction temperature is increased from 473 to 515 K, the relative amount of methane formed does not increase, but the maxi-

TABLE 2

Comparison of 10% Ni/COT and 10% Ni/P-25[a]

Catalyst	CO conversion (%)	Product distribution (mole%)						
		C_1	C_2	C_3	C_4	C_5	C_6	C_7+
10% Ni/COT	4.6	51.3	14.7	7.7	10.5	8.6	4.9	2.3
10% Ni/P-25	5.5	42.5	13.3	10.9	8.8	10.3	8.0	6.2

[a] $T = 200°C$, $H_2/CO = 3$, $P = 101$ kPa.

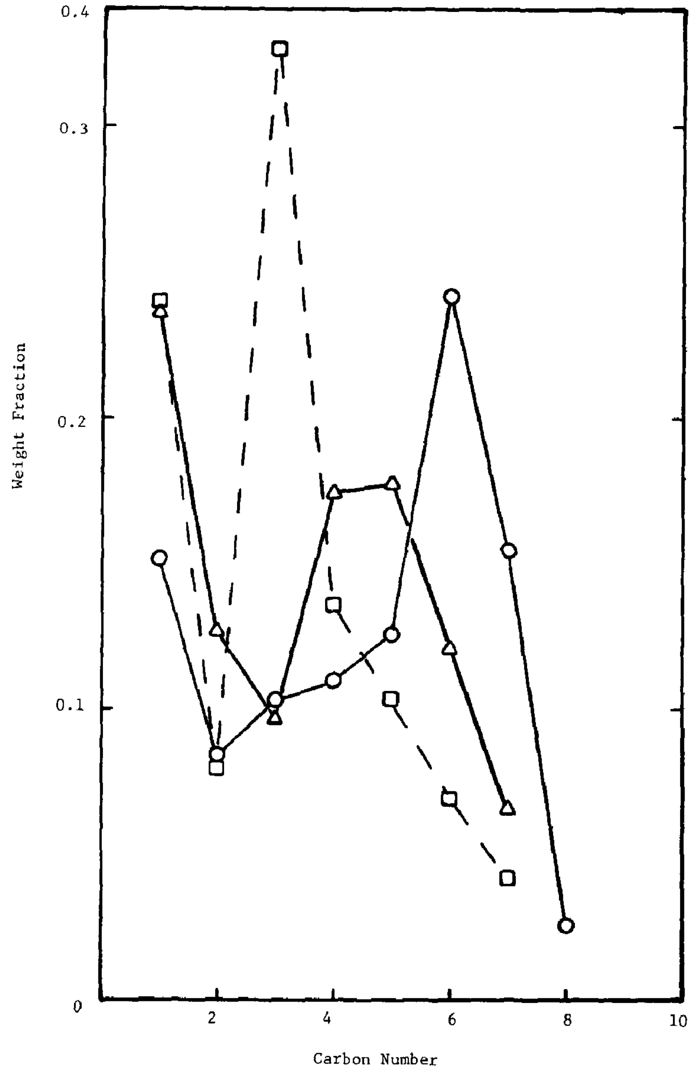

FIG. 1. Product distributions over 10% Ni/TiO_2 catalysts at $P = 101$ kPa and $H_2/CO = 3$; (△), COT, 473 K, 4.6% conversion; (□), COT, 515 K, 23.8% conversion; (○), P-25, 479 K, 9.6% conversion.

mum in the hydrocarbon distribution shifts from pentane to propane. The two runs at 473 (COT) and 479 K (P-25) show that the P-25 titania was more effective than COT in promoting chain-growth reactions and that the maximum was shifted to hexane over P-25 titania.

An intriguing aspect of the titania-supported nickel catalysts is that the enhanced chain-growth reaction does not appear to be adequately described by the simple polymerization models which have been applied to normal hydrocarbon products for many Fischer–Tropsch catalysts (*5–9*). If the chain-growth process conforms to a "normal" or "most probable distribution" (*9*), a plot of ln mole fraction (or wt%/C#) versus carbon number is linear. Based on limited available data, it appears that nickel on conventional supports such as Al_2O_3 or graphite produces a "normal distribution" except for methane. This is illustrated in Fig. 2. The high values for methane in the "normal distribution" plots are not unusual since many Fischer–Tropsch catalysts exhibit this characteristic (*9*, *10*).

The data in Table 2 for Ni/TiO_2 do not give a linear "normal distribution" plot as illustrated in Fig. 3. This is evidence that the chain-growth process is modified with Ni/TiO_2. Kibby and Kobylinski have recently shown that modified versions of the chain growth models can lead to product distributions which are significantly different from those expected for a "normal distribution" (*10*). These modifications allow for cracking reactions, chain initiation and propagation by ethylene, and variation in propagation rate with chain length. Cracking reactions can account for methane production greater than predicted by the "normal distribution" whereas reactions of ethylene can explain the lower than

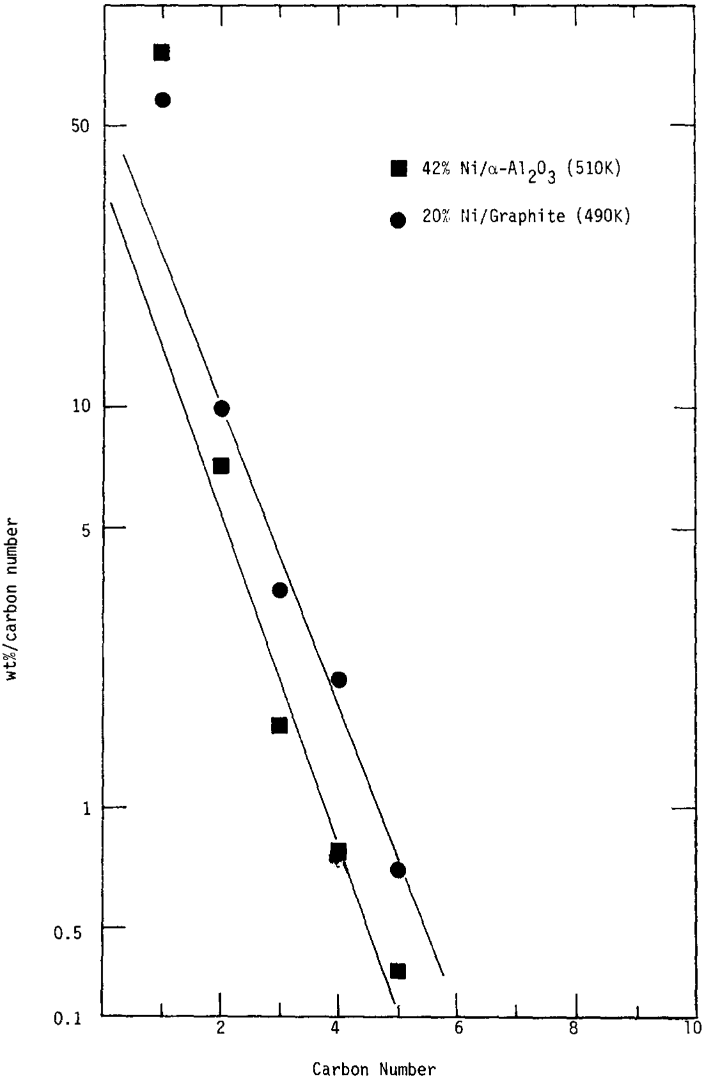

FIG. 2. "Normal distribution" plots of product distributions for supported nickel catalysts, P = 101 kPa, H_2/CO = 3. Catalysts are described in reference 4.

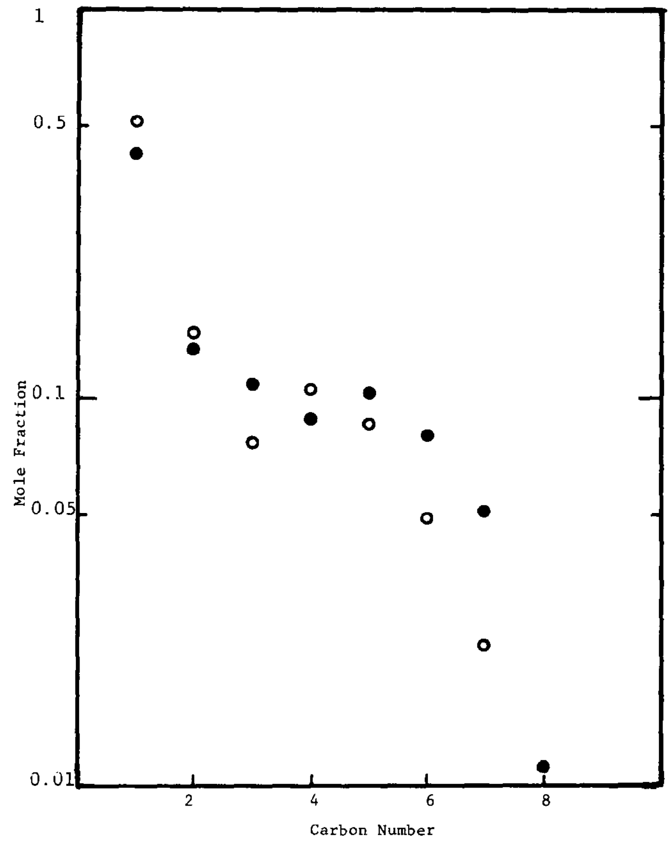

FIG. 3. "Normal distribution" plot of product distributions over 10% Ni/TiO$_2$ at 200°C; P = 101 kPa and H$_2$/CO = 3: (○), COT; (●), P-25.

expected C$_2$ fractions which are frequently found (*9, 11*). Propagation rates which are dependent on chain length can result in sharp peaks in the weight fraction distribution at particular carbon numbers. The patterns of product distribution of Ni/TiO$_2$ shown in Fig. 1 are very similar to patterns predicted by Kibby and Kobylinski for chain-length dependent propagation rates (*10*). Applying this interpretation to Ni/TiO$_2$, a significant decrease in propagation rates for C$_{3+}$ species at the higher temperature and C$_{6+}$ species at the lower temperature, relative to other carbon numbers, is indicated.

The detailed physical and chemical nature of the metal–support effect in Ni/TiO$_2$ catalysts which leads to the modification of catalytic properties is not known at the present time; however, one possibility may be ruled out. It does not appear likely that the TiO$_2$ surface itself becomes catalytically active to create a dual functional catalyst. This conclusion is based on the findings that titania alone is not active and a physical mixture of nickel powder and titania behaves like nickel powder alone. In addition, other group VIII metals on titania do not exhibit product distributions indicative of enhanced chain growth (*12*).

A number of reaction pathways have been proposed to account for the formation of higher molecular weight hydrocarbons from CO and H$_2$ (*13*), however, a single definitive mechanism has yet to be established. It is interesting to note, though, that both chemisorption measurements (*1*) and ir studies (*14*) indicate that the CO–Ni chemisorption bond is weakened for titania-supported nickel relative to supports such as Al_2O^3 and SiO_2. This would be expected to reduce CO dissociation and decrease the concentration of reactive surface carbon (*15*). Van Barneveld and Ponec have proposed that both molecularly adsorbed CO and reactive surface carbon are required for chain growth (*16*). The selectivity data for Ni/TiO_2 when considered together with the chemisorption and ir data provide support for the proposal of van Barneveld and Ponec.

In summary, the results provided by this study show that the support can alter the catalytic behavior of certain metals in CO/H_2 reactions. In addition, selectivities other than those dictated by simple polymerization kinetics appear to result from perturbations due to metal–support interactions. Although the nature of the interaction between nickel and titania is not well understood at this time, it is not unique to nickel. Titania-supported ruthenium also exhibits significantly different catalytic and adsorptive properties (*17*). Additional fundamental studies are required to better define the physical and chemical properties of these metal/titania systems and to increase our understanding of strong metal–support interactions.

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