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The Role of Surface Carbon in Catalytic Methanation[1]

For elucidation of the mechanism of catalytic methanation the adsorption of CO on nickel surfaces is of considerable importance. It has been the subject of a number of publications as reviewed by Ford (*1*). More recent studies with single crystals (*2-4*), and polycrystalline materials (*5*) have confirmed the earlier observations that the sorption process leads to the formation of CO admolecules on the surface of nickel without rupture of the C-O bond during adsorption. On heating, the adsorbed CO molecules desorb intact from several binding states on the nickel surface at $T < 450$ K. However, at $T > 450$ K exposure of these Ni crystal faces to CO results in the buildup of carbon on the solid surface (*6*). In addition, a surface reaction between carbon and oxygen adspecies, originally formed by the dissociative CO-chemisorption has been postulated (*7*). Similar observations were made on exposure of an evaporated nickel film to CO (*8*) at 460 K. In this case the formation of gaseous carbon dioxide was detected and attributed to the disproportionation reaction:

$$2CO \rightleftarrows C(s) + CO_2(g), \qquad (1)$$

where (s) refers to a surface species and (g) to a gas phase species. On an alumina-supported nickel catalyst (*9*), at temperatures as low as 350 K, the formation of carbon dioxide was noted and the interaction kinetics were interpreted in terms of reaction (1) and also the following reaction:

$$3Ni + 2CO \rightleftarrows Ni_3C + CO_2, \qquad (2)$$

i.e., the formation of a new bulk crystal phase represented by nickel carbide.

In recent studies with a dispersed nickel methanation catalyst on an alumina support we confirmed the formation of CO_2 as a result of reaction with CO at elevated temperatures. In order to evaluate the contribution of the carbon-forming reaction to methanation, an experiment was designed to measure quantitatively (a) the reaction of CO with the Ni/Al_2O_3 catalyst, (b) the reactivity towards hydrogen of the surface carbon species formed, and (c) the products resulting from this interaction.

A pulse microreactor was employed. In this system the operation of a multiport pulse valve permitted injection of constant-volume aliquots (~ 1 cm^3) of CO, H_2, or ($CO + H_2$) into a helium carrier stream that passed through a bed of nickel-on-alumina catalyst at $P = 50$ psig. The stream then entered a gas chromatograph (GC) where it was quantitatively analyzed for CO, CO_2, and CH_4. The column materials employed for gas chromatography consisted of Porapak T to separate CO from CO_2, and molecular sieve 5A to separate H_2, CO, and methane. Both columns were operated at 345 K. The catalyst bed consisted of 13.7 mg of hydrogen-reduced Girdler G-65 methanation catalyst (25 wt% Ni supported on Al_2O_3) crushed to finer than 200-mesh particle size. It rested on a Pyrex frit disc in the tubular glass reactor. Prior to any pulse experiments the catalyst was reduced for 15 hr at 725 K in a steady stream of pure H_2 at 1 atm, then purged for 1 hr in flowing He before the temperature was lowered to the level of interest in this study.

At 300 K only CO adsorption without disproportionation was observed.

$$CO(g) \rightarrow CO(s). \qquad (3)$$

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TABLE 1

Interaction of Hydrogen with Surface Carbon on Ni/Al_2O_3 Catalyst[a] at 553 K

Pulse[b]	Surface species deposited (moles × 10^6)			Gaseous products (moles × 10^6)		
	CO	C	ΣC	CH_4	CO_2	CO
CO	1.15	1.34	1.34	0	1.34	1.90
CO	0.41	0.67	2.01	0	0.67	3.98
H_2	0	0	0.05	1.96	0	0
CO	0.56	1.40	1.45	0	1.40	2.37
CO	0.27	0.67	2.12	0	0.67	4.12
H_2	0	0	0.02	2.10	0	0
CO	0.67	1.23	1.23	0	1.23	2.60
CO	0.13	0.64	1.87	0	0.64	4.32
CO	0.17	0.47	2.34	0	0.47	4.62
CO	0.20	0.39	2.73	0	0.39	4.75
CO	0.17	0.35	3.08	0	0.35	4.86
CO	0.31	0.32	3.40	0	0.32	4.78
H_2	0	0	0.01	3.39	0	0

[a] Mass of catalyst: 13.7 mg.

[b] CO pulse = 5.73×10^{-6} mole; H_2 pulse = 5.73×10^{-5} mole.

The total mass of CO adsorbed amounted to 1.14×10^{-4} moles CO/g of reduced catalyst, corresponding to a metal surface area of approximately 45 m^2/g Ni (on the assumption that each CO molecule interacts with two Ni surface atoms).

At 553 K, however, a temperature suitable for methanation catalysis with nickel, exposure of the catalyst to individual CO/He pulses and GC analysis of each pulse demonstrated the presence of CO_2 in the effluent. In accordance with the stoichiometry of reaction (1) the total number of moles of CO_2 produced is equal to the total number of moles of surface carbon, C(s), formed. Hence, by calibration of our aliquot volume and the gas chromatograph response to each of the gases in the mixture, we could measure (a) the amount of CO disproportionated, (b) the mass of C(s) formed, and (c) the quantity of CO chemisorbed on the catalyst (Table 1).

To ascertain the reactivity of the carbon species formed by chemisorption of CO on the catalyst surface, the freshly reduced catalyst was exposed to two CO pulses at 553 K. Then an aliquot of hydrogen was pulsed over the catalyst. Product analysis showed the presence of methane and unreacted hydrogen. The quantity of methane produced was almost exactly equal to the gram atoms of surface carbon deposited on the catalyst before the hydrogen pulse.

The results of several cycles of carbon deposition and methane formation are summarized in Table 1. It should be noted that the surface carbon resulting from six consecutive CO pulses can be rapidly and quantitatively converted to methane on exposure to a pulse of hydrogen. The mass balance between CH_4 and surface carbon is excellent, but no correlation exists between the chemisorbed CO and methane formed. The excess hydrogen hardly affects the CO adsorbed on the catalyst. Similar results for CH_4 formation from surface carbon were obtained at 625 K. However, when the catalyst was heated at 723 K for 10 min subsequent to carbon deposition at 553 K, deactivation of the surface carbon for methane formation occurred.

An additional series of pulse experiments was carried out in which the Ni/Al_2O_3 pretreated with different levels of surface carbon (attained by exposure to CO pulses) was brought in contact with pulses of CO/H_2 gas mixtures (10.4 vol% CO/89.6 vol% H_2). The results of these measurements are listed in Table 2. It should be noted that the total amount of methane produced is greatly augmented in the presence of surface carbon. As a matter of fact, at carbon levels less than 2×10^{-4}

TABLE 2

Contribution of Surface Carbon to Methane Formation[a]

Surface carbon (g atom × 10^6)	CH_4 yield (mole × 10^6)		
	From surface carbon	From CO	Total
0	0	5.25	5.25
3.08	2.90	5.11	8.01
3.86	3.22	4.93	8.15
7.53	3.22	3.51	6.73

[a] Catalyst G-65 (13.7 mg) at 553 K. Feed gas: 10.4 vol% CO/89.6 vol% H_2.

mole/g of catalyst, nearly all the carbon is converted to methane, so that the methane yield represents the sum of the carbon deposited and the CO converted in the blank experiment (Table 2). However, at higher surface densities of carbon the total conversion decreases, indicating the presence of additional carbon in a nonreactive form (for CH_4 production) which preempts some of the sites required for chemisorption of the reactants in the CO/H_2 pulse.

Our experimental results point to the existence of elemental surface carbon as an active precursor to methane formation by reaction with hydrogen on the nickel/alumina catalyst. To learn more about the nature of this carbon intermediate, we employed Auger electron spectroscopy to examine the surface of a catalyst sample after it had been exposed to an aliquot of CO at 553 K and cooled to room temperature in an He atmosphere. We detected carbidic-type carbon surface species. Further support for the existence of active carbon bound to the nickel atoms on the surface with a carbidic-type bond is provided by the loss in reactivity of the surface carbon following heating to 723 K, a treatment that converts the carbide to graphite (*10*), which is highly unreactive towards hydrogen (*11*).

A number of theoretical analyses have dealt with the interaction of CO with transition metal surfaces (*1*). Disproportionation of CO by reaction (1) is thermodynamically favored, but there is evidence that dissociative chemisorption also is feasible with the formation of a Ni–C and a Ni–O bond

$$2\text{Ni} + \text{CO} \rightarrow \text{Ni–C(s)} + \text{Ni–O(s)}. \quad (4)$$

From the dissociation energy of CO (256 kcal/mole) and the Ni–O bond strength (*12*) (89 kcal/mole) we may estimate the Ni–C binding energy to have a lower limit of 167 kcal/mole to make dissociative chemisorption of CO on Ni thermodynamically possible. A bond strength of this magnitude for Ni–C has been reported (*13*). By analogy with ruthenium, another well-known methanation catalyst, such a bond strength is realistic since the Ru–C binding energy is 151 kcal/mole (*14*).

Further evidence for dissociative adsorption of CO on Ni is provided by electron spectroscopy. In a study (*15*) of the photoelectron spectra of CO adsorbed on a polycrystalline nickel film at 300 K, a density-of-states distribution for the oxygen valence electrons was observed which could be attributed to CO(ads). However at $T > 400$ K, the density-of-states distribution changed to that characteristic of O(ads) resulting from CO breakup. Also, for CO adsorption on a disordered Ni(111) surface, Eastman and coworkers (*16*) reported rupture of the C–O bond, a process that became more difficult for the annealed crystal face.

We may conclude therefore that dissociative chemisorption of CO by contact with a nickel surface represents an energetically possible mechanism for the formation of the surface carbon intermediate in methanation catalysis. This carbon species, highly reactive towards hydrogenation and methane formation, should be distinguished from bulk nickel carbide, (Ni_3C), whose activity in methanation catalysis has been examined and found to be relatively low (*17–19*).

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