

FORMATION OF SURFACE CARBON AND METHANATION  
CATALYSIS ON ALUMINA SUPPORTED NICKEL

by

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ABSTRACT

The mechanism of catalytic methanation on an alumina-supported nickel catalyst (25 wt% Ni) has been examined by means of (1) kinetic studies with a pulse microreactor, (2) surface studies with Auger electron spectroscopy (AES), and (3) temperature programmed surface reaction kinetics (TPSR) at the gas/solid interface. During exposure of the catalyst to pulses of CO (diluted with He) at elevated temperatures ( $> 450$  K), we observed first-order formation of surface carbon. The surface carbon so formed exhibited high reactivity towards hydrogen with quantitative conversion to methane. The Auger electron spectra indicated that the surface carbon was bonded to the Ni as a carbidic-type surface species which converted to graphitic carbon of very low reactivity towards hydrogen at temperatures above 675 K. The kinetics of methane formation from surface carbon and gaseous  $H_2$  were determined by means of TPSR. The formation of  $CH_4$  is observed at temperatures as low as 375 K. The rates of methane formation follow first-order kinetics with respect to surface carbon. The activation energy for this process is 17.6 kcal/mol. The experimental data are analyzed in terms of a catalytic methanation mechanism in which dissociative adsorption of carbon monoxide and hydrogen is followed by reaction of surface carbon and surface oxygen with hydrogen adatoms to yield methane and water.

INTRODUCTION

In spite of considerable effort the methanation mechanism on nickel catalysts is not established unequivocally. At room temperature non-dissociative CO adsorption has been reported with the formation of several molecular bonding states on the surface of nickel.<sup>1-5</sup> However at elevated

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temperatures ( $> 350$  K) on an alumina-supported Ni catalyst<sup>6</sup> and on Ni films<sup>7</sup> the formation of  $\text{CO}_2$  was observed and the reaction interpreted in terms of disproportionation. More recently dissociative chemisorption<sup>8,9</sup> has been suggested in accordance with:



However the surface carbon so formed was considered to have negligible reactivity in methanation and to deactivate the catalyst with the formation of bulk  $\text{Ni}_3\text{C}$  or graphitic carbon structures.<sup>10</sup>

The objectives of our research were (1) the kinetics of interaction of CO with a  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst, (2) the reactivity of the surface carbon species toward hydrogen, and (3) the physical nature of the surface carbon and its bonding to Ni by Auger electron spectroscopy.

#### EXPERIMENTAL DETAILS

For measurement of the reaction of CO with the  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst a pulse-microreactor system was used operating at 50 psig. Constant-volume pulses ( $1.3 \text{ cm}^3$ ) of CO,  $\text{H}_2$ , or  $\text{CO}/\text{H}_2$  mixtures ( $\text{CO} + \text{H}_2$ ) in a helium carrier stream passed through the catalyst bed and entered a gas chromatograph (GC) for quantitative analysis ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ). The catalyst bed consisted of  $13.7 \times 10^{-3}$  g of hydrogen-reduced Girdler G-65 methanation catalyst (25 wt% Ni supported on  $\text{Al}_2\text{O}_3$ ) crushed to finer than 200-mesh particle size. The catalyst was reduced for 15 hours at 725 K in a steady stream of pure  $\text{H}_2$  at 1 atm, then purged for an hour in flowing He before the temperature was lowered to the desired operating level.

The rates of removal of the surface carbon species by hydrogen were determined by the technique of temperature programmed surface reaction (TPSR). This method represents a modification of the temperature programmed desorption technique (TPD) and is particularly well suited to the study of irreversible surface gas reactions, such as the interaction of hydrogen with surface carbon on nickel.<sup>11</sup> Interpretation of the experimental data in terms of kinetic parameters is based on the same theoretical analysis as employed in TPD.<sup>12</sup>

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\* (s) refers to a surface species and (g) to a gaseous species.

After depositing surface carbon on the catalyst (in the range from  $3 \times 10^{14}$  to  $9 \times 10^{14}$  atoms/cm<sup>2</sup> by exposure to a series of CO/He pulses at 450 - 550 K the sample was cooled to room temperature and the carrier gas changed to hydrogen. Subsequently the catalyst temperature was raised at a linear heating rate and the formation of methane resulting from the reaction of surface carbon with hydrogen was monitored as a function of time and temperature.

## EXPERIMENTAL RESULTS

### 1. Pulse Microreactor Experiments

To establish the reaction order with respect to CO for surface-carbon formation the CO concentration in the pulse contacting the catalyst sample in the microreactor was varied from 1.0 to 10.0 vol% CO (in He) at 553 K. From the amount of CO<sub>2</sub> formed the mass of carbon deposited on the catalyst surface could be calculated (Equations 2 and 3). From the difference between the CO consumed (equivalent to twice the amount of CO<sub>2</sub> formed) and the total CO lost from the pulse the amount of non-dissociated CO left on the catalyst could be determined. The results of a series of such experiments are shown in Figure 1. The data depicted by curve (a) demonstrate that the fractional conversion of CO to surface carbon is proportional to the amount of CO in the pulse, indicative of a first order surface reaction. Thus, rather than disproportionation the mechanism involves rapid CO adsorption and rate-limited dissociation of the CO admolecule (reaction 2), followed by rapid removal of the oxygen adatoms by further reaction with CO [reaction (3)].

Of interest is the quantitative conversion of the surface carbon to methane on exposure to a hydrogen pulse at 553 K (curve b, Figure 1), except at very high surface densities of carbon (an estimated surface coverage of more than 50 percent relative to Ni surface atoms) at which the amount of the carbon converted to methane is somewhat less than that deposited. Under these conditions the temperature-labile characteristics of the surface carbon become apparent, as discussed in further detail in the following section.

For a first-order reaction, such as the dissociative chemisorption of CO on Ni/Al<sub>2</sub>O<sub>3</sub>, a pulse-reactor experiment can be employed for kinetic studies. Thus, from measurement of the amount of surface carbon formed over a range of temperatures, the activation energy for this heterogeneous reaction can be evaluated.<sup>13</sup> Over a temperature range from 553 K to 613 K we calculate, an activation energy of 39 kcal/mole for reaction (3) on the basis of a heat of adsorption of CO on nickel<sup>7</sup> of -35.0 kcal/mole.

## 2. TPSR Studies

The rate of formation of  $\text{CH}_4$  by interaction of surface carbon with hydrogen, as studied by the TPSR technique, exhibits two distinct maxima (Figure 2). One methane peak is centered at  $430 \pm 20$  K ( $\alpha$  state), and the other at  $630 \pm 20$  K ( $\beta$  state). The ratio of carbon coverages between the two states was found to be  $N_\alpha/N_\beta = 2.5$  for exposure to CO at 523 K, and  $N_\alpha/N_\beta = 1.0$  for exposure at 575 K. The shape of the TPSR curve and the maximum reaction temperatures were not influenced significantly by the temperature of surface-carbon deposition (from 510 to 570 K). In addition, the lack of dependence of these parameters on initial carbon coverage provides strong evidence that the reaction under study is of first order in surface-carbon coverage.

The apparent activation energies for the reaction of hydrogen with both the  $\alpha$  and  $\beta$  states of adsorbed carbon were determined by varying the heating rate in a series of TPSR experiments.<sup>12</sup> Based on the theoretical analysis of a first-order surface reaction the apparent activation energies for the reaction of hydrogen with the  $\alpha$ - and  $\beta$ - states of surface carbon were calculated:

$$k_\alpha = 1.3 \times 10^7 \exp(-17700/RT) \text{ sec}^{-1} \quad (4)$$

$$k_\beta = 3.0 \times 10^9 \exp(-33000/RT) \text{ sec}^{-1} \quad (5)$$

## DISCUSSION

The experimental results strongly suggest the surface carbon formed by dissociative chemisorption of CO as an intermediate in the methanation reaction catalyzed by nickel. This mechanism is reinforced by experimental studies in which the surface carbon deposited to various degrees of surface coverage was exposed to pulses containing either hydrogen or mixtures of  $\text{H}_2$  and CO ( $\text{H}_2/\text{CO} = 9/1$ ). As summarized in Table 1 the surface carbon resulting from the exposure of the  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst to six consecutive CO pulses can be converted rapidly and quantitatively to methane on exposure to a pulse of hydrogen. The resulting carbon mass balance between methane and surface carbon is excellent. On contacting a catalyst containing surface carbon with a pulse of  $\text{H}_2/\text{CO}(9/1)$  the total amount of methane produced is greatly augmented over that measured on a clean nickel surface with the same gas mixture. As a matter of fact the total number of  $\text{CH}_4$  molecules formed approaches the sum of the number of carbon atoms deposited on the catalyst surface and the number of CO molecules converted in passing a  $\text{CO}/\text{H}_2$  pulse gas mixture over the clean catalyst (Table 1).

Furthermore it should be noted that in pulsing with CO some non-dissociated carbon monoxide is retained by the catalyst (Table 1). However these CO admolecules do not seem to contribute to methane formation on subsequent exposure to a pulse of H<sub>2</sub> at 553 K. This lack of participation of adsorbed CO molecules in methanation is substantiated by a calculation of the site occupancy of carbon and carbon monoxide adspecies on the catalyst surface resulting from exposure to pulses of different CO concentrations. In this analysis the assumption has been made that a bridge-bonded configuration [CO(B)] is particularly favorable for dissociative adsorption of CO, i.e., two neighboring nickel sites onto which CO is bound. The remaining sites are taken to be occupied by linearly bound CO admolecules [CO(L)], i.e., those bonded by sp-hybridized carbon to a single Ni atom. It will be noted from the data in Figure 1 (curve c) that during pulsing with progressively larger doses of CO, the finite number of Ni sites available is quickly preempted by CO(B) so that the adsorption of CO(L) goes through a maximum value. From a comparison of curves b and c in Figure 2 it is apparent that methane formation runs parallel to the surface density of C-atoms and not CO admolecules.

The chemical state of the carbon adatoms on the surface of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst has been determined by means of Auger electron spectroscopic studies. A catalyst sample exposed to several CO pulses (10 vol% in He) at 553 K and cooled to room temperature exhibited the spectrum shown in Figure 3. The Auger electrons with energies near 250 eV and 260 eV exhibited by the Ni/Al<sub>2</sub>O<sub>3</sub> sample and the carburized Ni foil are characteristic of a carbidic-type carbon structure.<sup>14,15</sup> The KLL Auger transition near 270 eV is common carbon in both the graphitic and the carbidic chemical states.

Since in the energy range of interest the Auger electrons emanate from a shallow depth near the surface of the solid (< 3 atomic layer) we may conclude that the dissociative chemisorption of CO on Ni results in the formation of a carbidic Ni-C surface bond. From the dissociation energy of CO (256 kcal/mole) and the Ni-O bond strength (89 kcal/mole) we estimate a value of 167 kcal/mole as the lower limit of the Ni-C binding energy required to make dissociative chemisorption of CO on Ni thermodynamically feasible. A bond strength of this magnitude for the Ni-C bond has been reported.<sup>16</sup>

Further evidence for dissociative adsorption of CO on Ni is provided by electron spectroscopy. In a study<sup>17</sup> 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 admolecules. However at T > 400 K, the density-of-states distribution changed to that characteristic of O-adatoms resulting

from CO dissociation. Also, for CO adsorption on a disordered Ni(111) surface, Eastman and coworkers<sup>18</sup> reported rupture of the C-O bond.

The labile characteristics of the carbidic surface carbon species on nickel becomes apparent during prolonged exposure of the catalyst surface to the electron beam of the Auger electron spectrometer or to elevated temperatures. Under these conditions the Auger spectrum indicates a gradual transformation of the carbidic carbon to the graphitic form, i.e. disappearance of the spectral fine structure associated with the 250 and 260 eV Auger "peaks" and growth of the signal intensity of the 270 eV "peak." This form of surface carbon is relatively unreactive toward hydrogen. Possibly it has the properties of the C( $\beta$ )-state (Figure 2) observed in the TPSR experiments. From the rate constants measured we would expect the reactivity of the graphitic carbon towards hydrogen to be 1/10,000 that of the carbidic species at 553 K.

Our experimental work strongly suggests the carbidic carbon surface species as an intermediate in the Ni-catalyzed methanation reaction. This surface carbon species, highly reactive towards hydrogenation and methane formation, should be distinguished from bulk nickel carbide, (Ni<sub>3</sub>C), whose activity in methanation catalysis has been examined and found to be relatively low.<sup>19-21</sup> The rate determining step is to be found in the dissociative chemisorption of CO. The activation energy for this process is estimated to be  $39 \pm 2$  kcal/mole, a value of the same magnitude found in our apparatus for steady state catalytic methanation at CO/H<sub>2</sub> = 1/9, as shown by the data in Figure 4.

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Table 1

INTERACTION OF H<sub>2</sub> AND H<sub>2</sub>/CO WITH SURFACE CARBON  
ON Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST<sup>a</sup> AT 553 K

Experiment	Pulse <sup>b</sup>		Total Number	Surface Species Deposited (moles x 10 <sup>6</sup> )		CH <sub>4</sub> Formed (mole x 10 <sup>6</sup> )
	Composition (vol%)			CO	C	
	H <sub>2</sub>	CO		CO	C	
1	0	10	2	1.56	2.01	-
	100	0	1	0	0	1.96
2	0	10	2	0.83	2.12	-
	100	0	1	0	0	2.10
3	0	10	6	1.65	3.40	-
	100	0	1	0	0	3.39
4	90	10	1	-	-	5.25
	0	10	5	-	3.08	-
	90	10	1	-	-	8.01

<sup>a</sup> Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Girdler G-65, 25 wt% Ni).

<sup>b</sup> CO pulse = 5.73 x 10<sup>-6</sup> mole; H<sub>2</sub> pulse = 5.73 x 10<sup>-5</sup> mole.

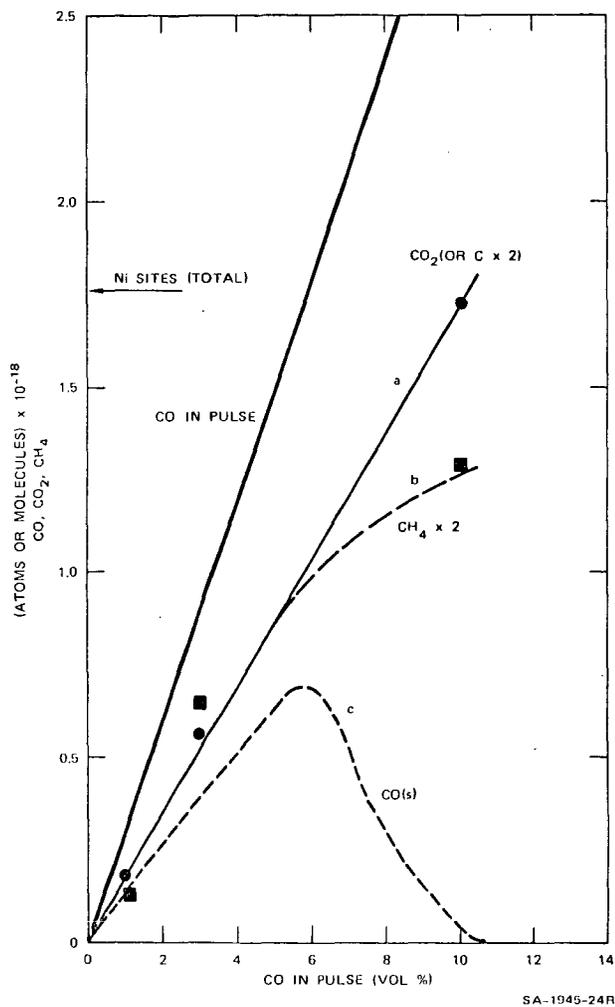


FIGURE 1 SURFACE CARBON INTERMEDIATE IN CATALYTIC METHANATION ( $\text{Ni}/\text{Al}_2\text{O}_3$ , 25 wt %)

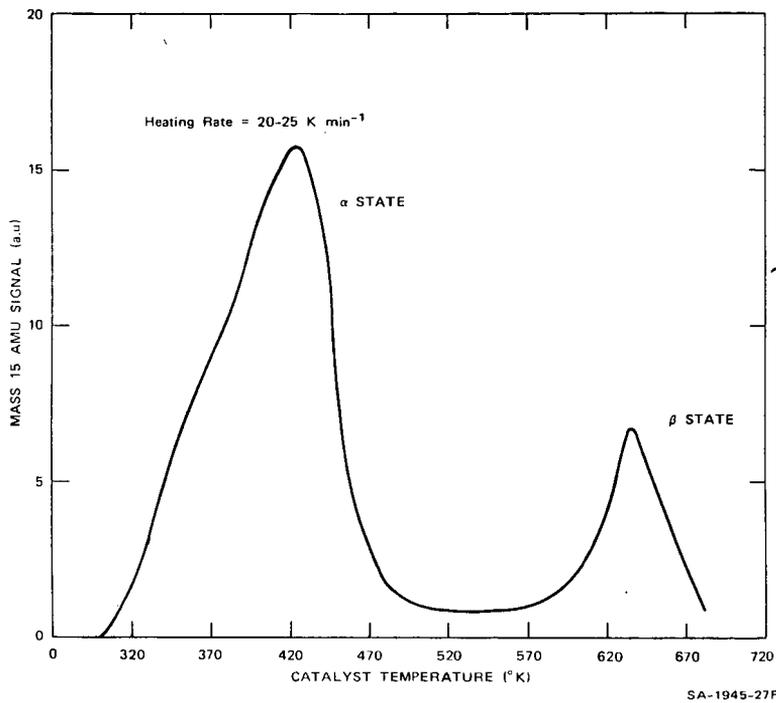
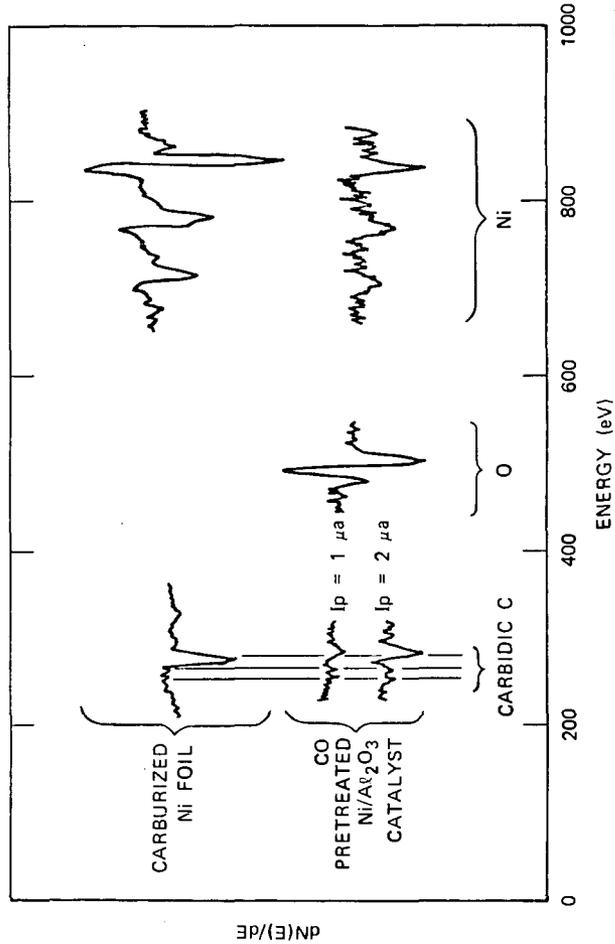


FIGURE 2 TEMPERATURE PROGRAMMED SURFACE REACTION BETWEEN SURFACE CARBON AND GASEOUS HYDROGEN CATALYZED BY Ni/Al<sub>2</sub>O<sub>3</sub> (25 wt %)



SA-4387-6

FIGURE 3 AES OF SURFACE CARBON MINI/Al<sub>2</sub>O<sub>3</sub> CATALYST AFTER EXPOSURE TO CO AT 553 K

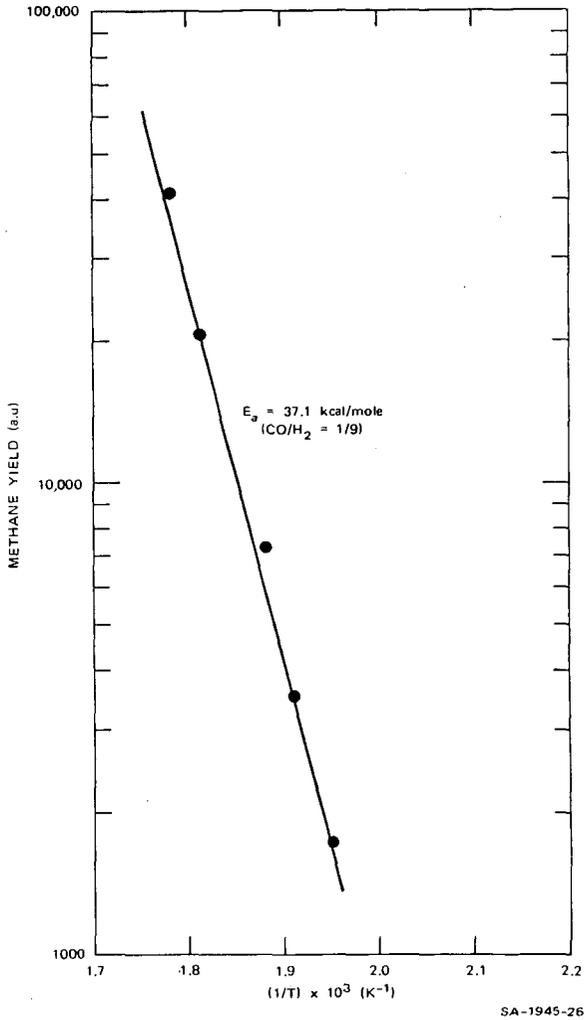


FIGURE 4 STEADY STATE METHANATION ACTIVITY OF Ni/Al<sub>2</sub>O<sub>3</sub> (25 wt %)