

CATALYTIC METHANATION OVER SINGLE CRYSTAL NICKEL AND RUTHENIUM:
REACTION KINETICS ON DIFFERENT CRYSTAL PLANES

R. D. Kelley and D. Wayne Goodman

Surface Science Division

National Bureau of Standards

Washington, D.C. 20234

Introduction

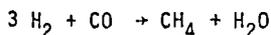
A specially designed ultrahigh vacuum system has been used to study the kinetics of the hydrogenation of CO over low surface area, single crystal catalysts. In a recent publication (1), we have reported reaction rate measurements for a Ni(100) catalyst and compared those results with kinetic data, derived from the literature, for small particle Ni supported on Al_2O_3 . There was remarkable agreement between the two catalyst systems in regard to specific reaction rates (the rate normalized to the number of surface metal atoms), the activation energy, and the product distribution. In the present report, we compare reaction rates measured on two crystal planes of Ni--the (100) and the close-packed (111)--and two crystal planes of Ru--the zig-zag, open (110) and the close packed (001). We also report the variation of the reaction rate and the surface carbon concentration with total pressure and with the $H_2:CO$ ratio. The surface carbon concentration (an active "carbide" carbon species) varies with the total pressure and with the reactant gas ratio. A striking correlation has been found between the surface carbide level and the catalytic reaction rate.

Experimental

The apparatus used for these studies consists of two connected ultrahigh vacuum chambers--one for surface analysis (Auger Electron Spectroscopy (AES)) and the other suitable for high pressure catalytic rate studies. A detailed description of the apparatus, the crystal cleaning procedure, and the techniques used to obtain kinetic rate data have been published (1). It should be noted that the number of metal surface atoms exposed to the reactant gas (used to normalize reaction rate data) is derived from the geometrical surface area of the annealed crystal and the appropriate surface atom density [Ni(100): 1.562×10^{15} atoms/cm²; Ni(111): 1.586×10^{15} atoms/cm²; Ru(110): 1.00×10^{15} atoms/cm²; Ru(001): 1.58×10^{15} atoms/cm²]. The Ru samples were cleaned using high temperature oxidation at 10^{-8} torr (2) followed by heating in vacuum to 1570K. (2)

Results and Discussion

The observation (1) that the rate of the reaction



(expressed as CH_4 molecules/surface site/sec) measured over a low surface area, single crystal catalyst is nearly identical to that measured over a supported small particle Ni catalyst (2) is a strong indication that there is little reactivity difference between those crystal planes commonly found in polycrystalline material (i.e., the low index planes). This expectation is confirmed in the data presented in Fig. 1, which is a plot of the specific rate (or turnover number) of CH_4 production versus the reciprocal temperature. The similarity between the open (100) and the close-packed (111) crystal planes of Ni is evident in both the value of the specific rate and the activation energy (24.7 kcal mole⁻¹ derived from the Ni(100) data). For comparison three sets of data for nickel (supported on alumina) catalysts are replotted from the literature. Thus for the $\text{H}_2 + \text{CO}$ reaction over Ni, there is essentially no variation in the reaction rate as the catalyst changes from small metal particles to bulk single crystal planes.

Analysis of an active crystal catalyst surface with AES indicates a low level of a carbon species and the absence of oxygen (1). Measurements of the rate of production of this surface carbon species (in pure CO) and the rate of reaction (in pure H_2) have indicated that both processes (i.e., the production and the removal of the surface carbon species) proceed at very similar rates. (3) A mechanism for the $\text{H}_2 + \text{CO}$ reaction consistent with the kinetic data and the finite surface carbon level during reaction was developed which involves the hydrogenation of an active carbon species formed from the dissociation of CO. Fig. 2a shows the changes in the reaction rate as the pressure is increased from 1-120 torr at a fixed $\text{H}_2:\text{CO}$ ratio. At low temperatures the rates fall on the same straight line at all pressures. As the temperature is increased a deviation from linearity is seen--the higher the pressure the higher the deviation temperature. Accompanying this non-linear rate behavior is an increase in the active carbon level on the surface of the catalyst crystal. We have proposed that this behavior (the departure from the linearity of the rate in Fig. 2a and the accompanying increase in the surface carbon level) is due to a decrease in the surface coverage of hydrogen and thus a decrease in the rate of hydrogenation of surface carbon. Fig. 2b shows similar data for a Ru(110) crystal. The variation of the reaction rate with pressure is very similar to the Ni(100) crystal--i.e., a departure from linearity of the rate and accompanying this departure an increase in the surface carbon level (see reference (4) for details of the AES measurement of carbon on Ru). We presume that the explanation of this behavior is the same offered for the Ni crystal. In fact, since the binding energy of H on Ru is lower than on Ni (2) the deviation from linearity should be expected at a lower temperature. This is particularly evident in the 1 torr data of Fig. 2a and 2b.

In addition to the rate data for the Ru(110) crystal, Fig. 2b also contains limited data for the basal plane of ruthenium, Ru(001). While the comparison is limited, it is clear that the $H_2 + CO$ reaction is quite similar in regard to the specific reaction rate and the activation energy for these two crystal planes of ruthenium.

The data of Fig. 2 indicate that the effect of the total pressure on the reaction rate is dependent on the temperature at which the measurements are made. Fig. 3 shows the variation of the specific rate as a function of pressure at two temperatures over a Ni(100) catalyst with the $H_2/CO = 4$. Many authors (5) have fitted reaction rate variation with pressure to a power rate law of the form

$$R_{CH_4} = A e^{-E/RT} p_{H_2}^x p_{CO}^y \quad 1)$$

The exponents, fitted from experimental data, have been used to derive information about the reaction mechanism (6). It is clear from Fig. 3 that, while power rate law exponents can be derived and used to scale rate data at fixed reaction conditions, such exponents are very sensitive to the reaction temperature. It is doubtful that any fundamental significance can be attached to values of the exponents derived at one temperature.

We have attempted to determine the dependence of the methanation rate on the partial pressure of both H_2 and CO . In conducting this study, we have measured the rate of CH_4 production with $H_2:CO$ ratios which varied from 0.1 to 1000 and with a total pressure which varied from 1 to 1500 torr. The results of this study indicate that even at one temperature a power rate law such as equation 1 is not adequate to describe the partial pressure dependence of the reaction rate. However, all reaction rate data measured over a Ni(100) catalyst can be correlated, on a smooth curve, with the concentration of "active" carbon on the Ni surface. Figure 4 is a plot of the measured carbon surface coverage and the measured specific reaction rate for various $H_2:CO$ ratios and total pressures at a temperature of 625K. It should be noted that the reaction rates are steady-state rates with no evidence for deactivation and that the carbon AES lineshape is always that of a "carbide" with no evidence for graphite formation. The estimate of carbon surface coverage from the AES carbon intensity is based on AES data obtained from a CO monolayer (4).

Since there is no pressure effect--in the pressure range of these measurements--in the rate of carbide production from pure CO (3) and since

at any $H_2:CO$ ratio an increase in pressure results in a decrease in surface carbon, we conclude that the data of Figure 4 is a manifestation of the change in the hydrogenation rate of the surface carbide with total pressure and with the $H_2:CO$ ratio. We have previously concluded (1) that the methanation reaction rate is determined by a delicate balance of the formation and removal of surface carbide and that neither of these processes are rate determining in the usual sense. Thus, as indicated in Figure 4 under reaction conditions unfavorable for the hydrogenation rate (e.g., low partial pressure of H_2 at a high temperature) the reaction rate should decrease and be accompanied by an increase in the surface carbon level. At lower temperatures the surface concentration of hydrogen (and thus the hydrogenation rate) becomes less strongly dependent on pressure. For example, the rate of CH_4 production for a 4:1 $H_2:CO$ ratio at 503K (plotted in Fig. 3) is only slightly dependent on pressure (from 1-1500 torr). The measured surface carbon level under these conditions is approximately 10% of a monolayer and does not change significantly over the entire pressure range.

Thus it appears that changes in temperature, H_2/CO ratio, and total pressure have a common effect on the methanation rate--namely, to change the surface concentration of hydrogen. Although these effects have been observed predominately on the Ni(100) crystal, the similarities between Ni and Ru with regard to reaction rate variation with pressure and with surface carbide level (Fig. 2) strongly suggest a similar explanation for ruthenium.

The results of these pressure studies suggest considerable caution in drawing the conclusion that crystallographic effects are absent in the methanation reaction over Ni or Ru. While this result appears valid under reaction conditions in which surface carbide level is low, as reaction conditions change effects due to diffusion of carbon, stability of the surface carbide, hydrogen surface concentration and other effects which can have a strong crystallographic dependence can become dominant factors influencing the reactivity.

FIGURE CAPTIONS

- Figure 1. Arrhenius plot comparing CH_4 synthesis on Ni(100), Ni(111), and supported Ni catalysts. Reaction conditions: 120 torr, $\text{H}_2/\text{CO} = 4$. Ni(111) - this work; Ni(100) - ref. (1); supported Ni - ref. 7.
- Figure 2. a.) Arrhenius plot of CH_4 synthesis on a Ni(100) catalyst at total reactant pressures of 1, 10, 120 torr. $\text{H}_2/\text{CO} = 4$.
b.) Arrhenius plot of CH_4 synthesis on a Ru(110) catalyst at total reactant pressures of 1, 10, 120 torr. $\text{H}_2/\text{CO} = 4$. Data at two temperatures for a Ru(001) catalyst at 120 torr is plotted with the symbol, x.
- Figure 3. Methane production rate (molecules/surface site/sec) versus pressure at 503K and 625K over a Ni(100) catalyst.
- Figure 4. Methane production rate (molecules/surface site/sec) at 625K over a Ni(100) catalyst versus surface carbon concentration (under steady state reaction conditions). The H_2/CO ratio and the total pressure (torr) for each point plotted is indicated in the insert.

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Fig. 1

Comparison of Rate of CH₄ Synthesis Over Ni Catalysts

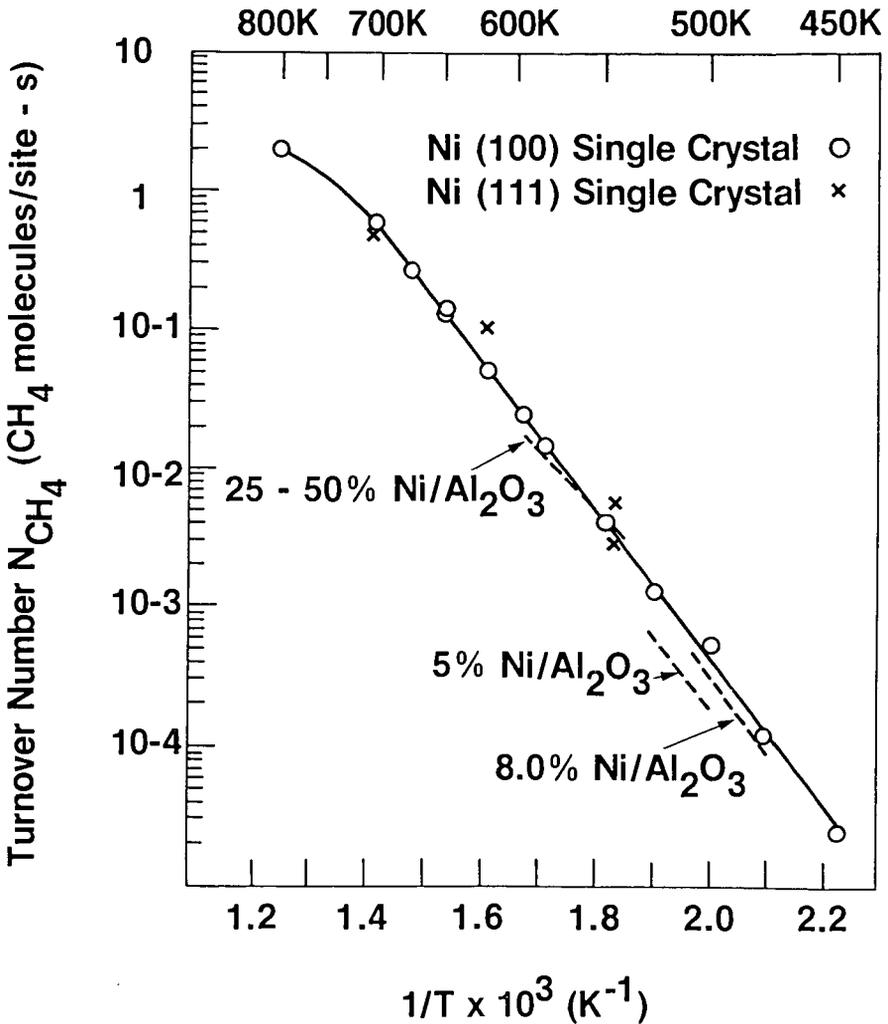


Fig. 2

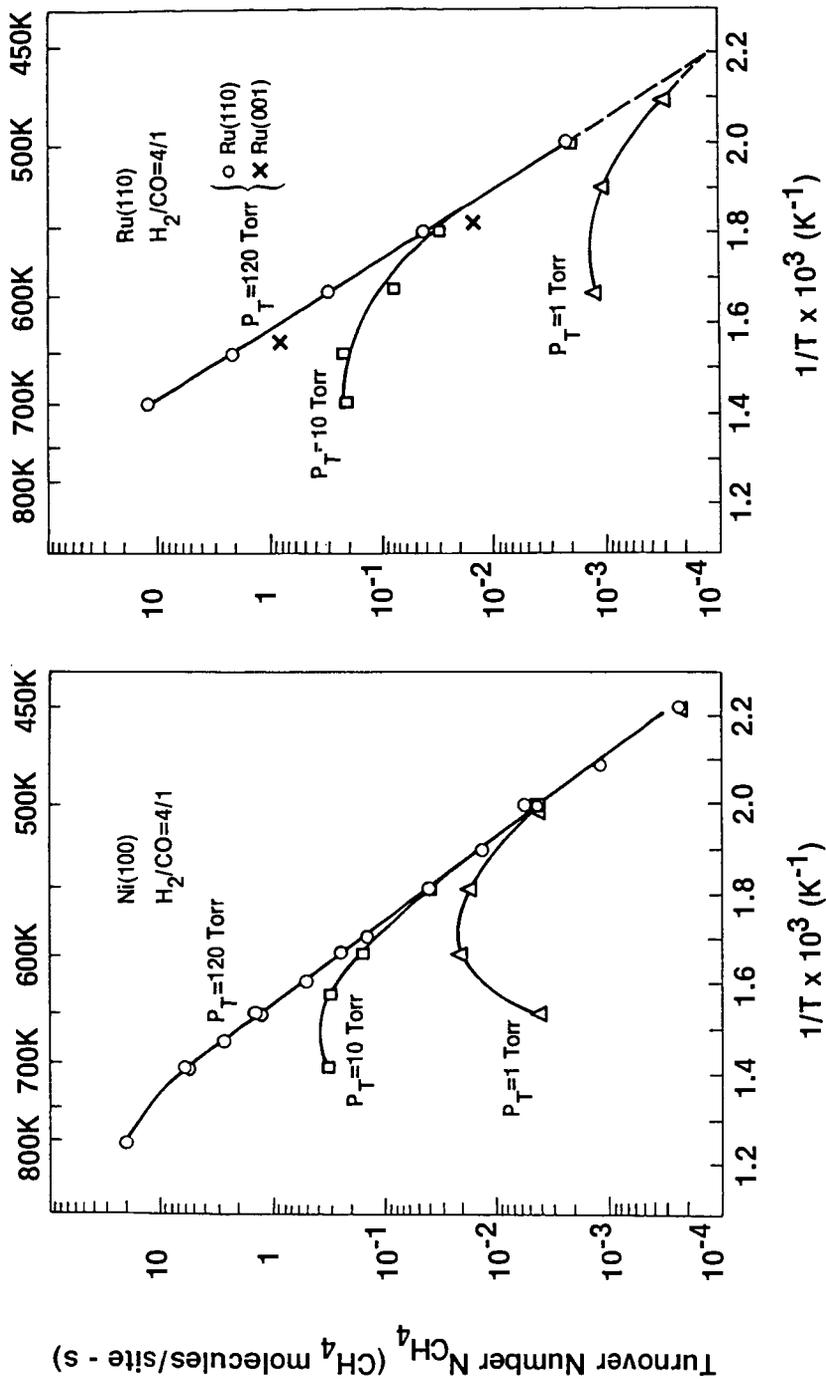


Fig. 3

Methane Production Versus Pressure Over A Ni(100) Catalyst

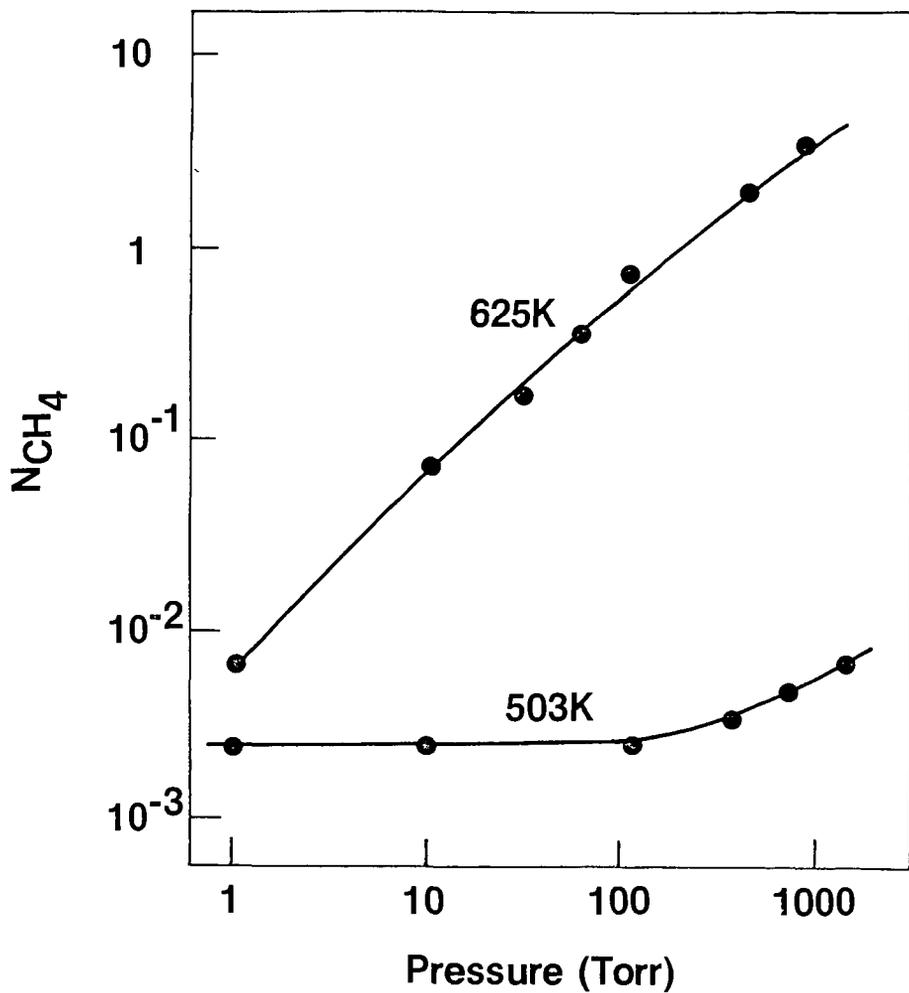


Fig. 4

Methanation Rate Versus Surface Carbon Level

