## SURFACE SCIENCE LETTERS

## CATALYTIC METHANATION OVER SINGLE CRYSTAL NICKEL AND RUTHENIUM: REACTION KINETICS ON DIFFERENT CRYSTAL PLANES AND THE CORRELATION OF SURFACE CARBIDE CONCENTRATION WITH REACTION RATE

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The kinetics of the reaction of  $H_2$  and CO over single crystals of nickel ((100) and (111)) and ruthenium ((110) and (001)) have been studied as a function of pressure and  $H_2$ /CO ratio. A striking correlation has been observed between the measured surface carbide concentration and the rate of methane production while varying the  $H_2$ /CO ratio and the total pressure. This correlation is shown to be a necessary consequence of the reaction mechanism previously proposed [1] for the catalytic methanation reaction over nickel.

In a previous publication [1], we have reported reaction rate measurements of the hydrogenation of CO on 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 with respect 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). The surface carbon concentration (an active "carbidic" carbon species) varies substantially with total pressure and reactant gas ratio. A striking correlation has been found between the surface carbide level and the catalytic reaction rate. This correlation of a measured concentration of surface species with the catalytic reaction rate is entirely consistent with the reaction mechanism proposed [1] for the production of CH<sub>4</sub>, i.e., a balance between two independent processes - the dissociation of CO and the reaction of the resulting carbide with surface hydrogen atoms.

The apparatus used for these studies consists of two connected ultra-high

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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 procedures, 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):  $1.62 \times 10^{15}$  atoms/cm<sup>2</sup>; Ni(111):  $1.86 \times 10^{15}$  atoms/cm<sup>2</sup>; Ru(110):  $1.00 \times 10^{15}$  atoms/cm<sup>2</sup>; Ru(001):  $1.58 \times 10^{15}$  atoms/cm<sup>2</sup>). The Ru samples were cleaned using high temperature oxidation at  $10^{-6}$  Torr O<sub>2</sub> followed by heating in vacuum to 1570 K [3].

The observation that the overall rate of the reaction

 $3 \text{ H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O},$ 

expressed as  $CH_4$  molecules/Ni surface atom  $\cdot$  s, measured over a low surface area, single crystal catalyst (Ni(100)) is nearly identical to that measured over a supported small particle Ni catalyst [1] provides strong evidence there is little reactivity difference between those crystal planes thermodynamically favored in thermally annealed polycrystalline material (i.e., the low index planes). This



Fig. 1. Arrhenius plot comparing  $CH_4$  synthesis on Ni(100), Ni(111), and supported Ni catalysts. Reaction conditions: 120 Torr, the ratio  $H_2$ :CO is 4. Ni(111), this work; Ni(100), ref. [1]; supported Ni, ref. [8].

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 reciprocal temperature. The similarity between the open (100) and the more 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<sup>-1</sup> derived from the Ni(100) data). For comparison three sets of data for nickel (supported on alumina) catalysts are replotted from the literature. Kao, Tsai and Chung [2], using techniques similar to those employed in this study, have recently measured the specific rate of  $CH_4$  formation, the activation energy and the product distribution for the  $H_2/CO$  reaction on a Ni(111) catalyst. Their results are in remarkably good agreement (better than 20% for  $CH_4$  production in the temperature range 443–543 K) with those reported here. Thus for the  $H_2$  + 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 following reaction 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 its removal in pure  $H_2$  have demonstrated that both processes proceed at very similar rates [4]. A mechanism for the  $H_2 + CO$ reaction consistent with the kinetic data and the finite surface carbon level during reaction was developed [1] which involves the hydrogenation of an



Fig. 2. (a) Arrhenius plot of CH<sub>4</sub> synthesis on a Ni(100) catalyst at total reactant pressures of 1, 10 and 120 Torr. The ratio H<sub>2</sub>: CO is 4. (b) Arrhenius plot of CH<sub>4</sub> synthesis on a Ru(110) catalyst at total reactant pressures of 1, 10 and 120 Torr. The ratio H<sub>2</sub>: CO is 4. Data at two temperatures for a Ru(001) catalyst at 120 Torr are plotted with the symbol  $\times$ .

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 H<sub>2</sub>: 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 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 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 ref. [5] 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 [3] the deviation from linearity should be expected at a lower temperature. This is particularly evident in the 1 Torr data of figs. 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<sub>2</sub> + CO reaction is quite similar in regard to the specific reaction rate and the activation energy for these two crystal planes of ruthenium. The difference in surface structure between these two ruthenium planes is considerably greater than between the two crystal facets of Ni.

In the absence of surface sulfur, deactivation of the catalyst crystal is *always* accompanied by the appearance of graphite on the catalyst surface. On the Ni(100) crystal, graphite is only observed [4] when two conditions are met: (a) the surface carbide level is at the saturation level of 0.50 monolayer and (b) the crystal temperature exceeds a critical temperature ( $\sim 650$  K). Deactivation of a ruthenium crystal is very similar to that of nickel, differing only in the carbide level and the critical temperature at which graphite is observed.

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. We have shown (fig. 8, ref. [1]) that at 503 K the methanation rate is insensitive to the pressure of a 4:1 H<sub>2</sub>-CO mixture and that the surface carbon level is essentially constant. However at 625 K both the specific reaction rate and the surface carbon level are very sensitive to the gas pressure. Many authors [6] have fitted reaction rate variation with pressure to a power rate law of the form

$$R_{\rm CH_4} = A \ e^{-E/RT} \ P_{\rm H_2}^{\rm x} P_{\rm CO}^{\rm y}. \tag{1}$$

The exponents in the pressure terms are derived from experimental data and

are frequently used to distinguish between proposed reaction mechanisms [7]. It is clear from fig. 2 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 eq. (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. Fig. 3 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 625 K. 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.



Fig. 3. Methane production rate (molecules/Ni surface atom s) at 625 K 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 are indicated in the insert.

Since there is no pressure effect (in the pressure range of these measurements) in the rate of carbide production from pure CO [4], 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 fig. 3 are a manifestation of the change in the surface hydrogen atom concentration (and consequently 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 between the formation and removal of surface carbide and that neither of these processes are rate determining in the usual sense. Thus, as indicated in fig. 4 under reaction conditions unfavorable for the hydrogenation rate (e.g., low partial pressure of H<sub>2</sub> 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 503 K is only slightly dependent on pressure (from 1-1500 Torr) [1]. 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 strongly suggest a similar explanation for ruthenium. In fact, reaction rate measurements coupled with surface analysis on polycrystalline and single crystal iron [10] shows such remarkedly similar behavior to that on Ni and Ru that the detailed observations reported here for Ni(100) may be extended to most of the transition metals of interests in methanation and Fischer–Tropsch catalysis. A similar study on Ni(100) detailing the change in higher hydrocarbon reaction rates with changes in steady-state surface carbide concentration will be reported shortly.

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