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NOTES

Measurement of Carbide Buildup and Removal Kinetics on Ni(100)

The catalytic methanation reaction ($3H_2 + CO \rightarrow CH_4 + H_2O$) over transition metal catalysts has recently been a subject of intense interest (*1*, *2*). The connection between specific rate measurements for this reaction over a single crystal Ni(100) surface and over supported Ni catalyst has been established (*3*) and lends support to the notion that studies involving well-characterized single crystal surfaces are indeed readily relatable to those using supported materials. In the course of these and other studies on unsupported Fe (*4*), Rh (*5*), Ru (*6*), and Ni (*7*) as well as on supported Ni (*8*) and Ru (*9*), the dissociation of CO has been implicated as one step in the methanation reaction. The surface carbon produced in this manner has an Auger (AES) spectrum characteristic of bulk carbides (*10*) and has been designated carbidic carbon (*3*).

The role of surface carbon in catalytic methanation has long been a subject of intense interest (*11*). Therefore, it is of considerable importance to measure the specific rates of formation and hydrogenation of this carbidic carbon. Such measurements on Ni(100) form the basis of this paper.

The experiments were done with a combined reactor-UHV analysis chamber described previously (*3*). Using a Ni(100) surface, cleaned by standard procedures (*3*), the rate of carbide buildup at various temperatures was measured as follows: (1) Surface cleanliness was established by AES. (2) The sample was then retracted into the reaction chamber and exposed to 24 Torr of CO for various times and temperatures. (3) After evacuation the sample was transferred to the UHV chamber and flashed briefly to 600°K to remove residual CO, and (4) the AES spectra of C and Ni were measured. Previous thermal desorption studies (*12*) have shown that desorption of a monolayer of CO from Ni(100) by heating to 600°K does not produce detectable carbon residue.

A summary of the carbon buildup results is shown in Fig. 1 as the relative carbon AES signal [normalized to the Ni(848 eV) transition] versus reaction time. Several features are noteworthy: (a) There are two carbon regions characterized by different Auger line-shapes (*3*), a carbide region ordinate values less than 0.28 and a graphite region for larger ordinates. Auger studies with low electron beam currents on a monolayer coverage of CO indicate that the saturation coverage of carbide at 600°K corresponds to approximately one-half monolayer. (b) The carbon signals are reproducible, well-behaved, and depend on

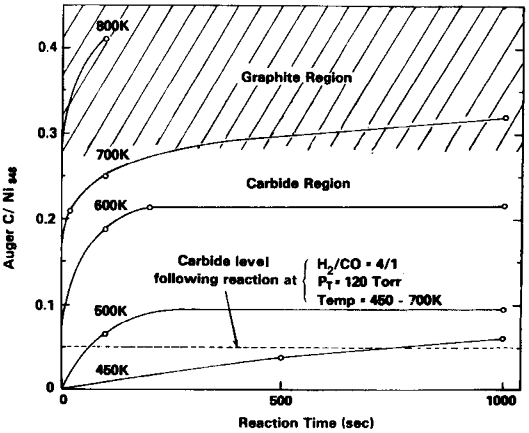

FIG. 1. The rate of carbon buildup on a Ni(100) catalyst by reaction with 24 Torr CO. Ordinate values for carbon have been normalized to the Ni 848 Auger transition intensity.

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both reaction time and temperature. (c) The apparent saturation carbide level increases with temperature between 500 and 700°K. (d) Entry into the graphite region occurs only after a certain level of carbide accumulates, and (e) entry into the graphite region is not possible on the time scale of these experiments for $T < 650$°K.

The horizontal dashed line of Fig. 1 marks the carbide level observed after a methanation reaction experiment at $H_2/CO = 4$, a total pressure of 120 Torr, and any temperature between 450 and 700°K. We assume this is the operating steady-state carbide level during the reaction. From the data at 450 and 500°K we estimate the apparent activation energy, at the steady-state carbon level, to lie between 22 and 25 kcal mole^{-1}. This is to be compared with the overall methanation activation energy of 24.7 kcal mole^{-1} (*3*). More significantly, the data at 450°K gives a turnover number for carbide formation, at the operating steady-state level, of 2×10^{-4} compared to 3×10^{-4} for methane formation (*3*).

In Fig. 2, the carbide level as a function of reaction time in 100 Torr of H_2 is shown. At each temperature shown, the Ni(100) surface was precarbided by exposure to CO at 600°K and then treated with hydrogen in the reaction chamber for various times. Steps (3) and (4) above were then followed to measure the carbide level. *In vacuo* heating of the carbide for 1000 sec produced no significant changes in Auger line shape or amplitude until temperatures in excess of 850°K were reached.

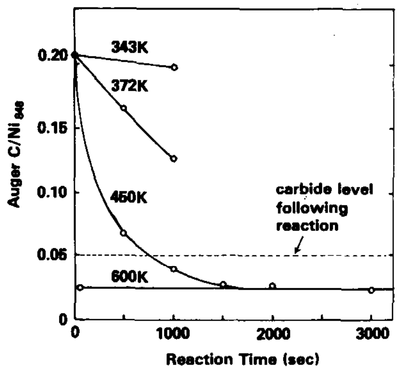

FIG. 2. The rate of carbide removal by reaction with 100 Torr hydrogen. At each temperature shown, the Ni(100) surface was precarbided by exposure to 24 Torr CO at 600°K and then treated with hydrogen.

Figure 2 indicates that: (1) The rate of carbide removal is a strong function of the reaction temperature and (2) there is an asymptotic carbide level of about $\frac{1}{10}$ the saturation coverage. The horizontal dotted line in Fig. 2 shows the operating steady-state carbide level during the methanation reaction under the same conditions as in Fig. 1. The turnover number for carbide removal calculated from the slope of the 450°K curve (at the operating carbide level) is 2×10^{-4} compared to the carbide formation (2×10^{-4}) and methane formation (3×10^{-4}). From the data at 343 and 372°K the activation energy for carbide hydrogenation, at saturation carbide coverage, is 21 kcal mole^{-1}. No estimate can be made for the activation energy for carbide hydrogenation at the operating carbide level. However, the observation of a constant carbide coverage under reaction conditions over the temperature range 450–750°K (*3*) suggests that the activation energy of carbide hydrogenation is very near that for the carbide formation. From these data we conclude that at 450°K the turnover numbers for methane formation in a 4/1 H_2–CO mixture at 120 Torr, carbide formation in pure CO (24 Torr), and carbide hydrogenation in pure H_2 (100 Torr) are very nearly the same. Thus in a H_2–CO atmosphere the reaction rate is determined by a delicate balance of the formation and removal steps and neither of these is rate determining in the usual sense, predictably the surface carbon level has been observed to be particularly sensitive to reaction parameters such as hydrogen partial pressure and temperature. This has important implications for methanation catalyzed by Ni. A detailed discussion of these kinetics and comparable data for Ru will be published separately (*6*).

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