Hydrogenation of Carbon Monoxide on Mo(100) Single Crystals and Polycrystalline Foils

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The hydrogenation of carbon monoxide over (100)-oriented single crystals and polycrystalline molybdenum catalysts produces primarily methane, ethene, and propene. The rates of formation of all products were found to be the same for both the (100) single crystals and polycrystalline foils suggesting that the reaction is structure insensitive. The dependence of the rate of formation of methane on reactant pressure was found to be $r_{CH_4} = KP_{CO}^{+0.32\pm0.05}P_{H_2}^{+1.0\pm0.1}$. The unusual positive CO pressure dependence points to a mechanism of methanation that is different from that on other transition metal methanation catalysts (Fe, Ru, Ni) although the activation energy for the reaction is similar, 24 kcal/mol. Addition of K to the surface, at coverages of less than 0.3 ML, increased the overall rate of reaction and enhanced the olefin-to-paraffin ratio. The addition of S to the surface decreases the rate of hydrogenation but, for coverages up to ~0.25 ML, increases the ratio of ethene to methane by a factor of as much as 5. © 1985 Academic Press, Inc.

INTRODUCTION

Many transition metals have been investigated as catalysts for the hydrogenation of CO, but, until recently, very little work had been carried out using Mo (*1–4*). The research studies that have been performed, however, already point to several interesting and unique characteristics of Mo catalysts. Workers at the U.S. Bureau of Mines reported (*1*) that molybdenum catalysts had high activity for methane production although not as high as Fe, Ni, Co, and Ru. Saito and Anderson (*2, 3*) extended these studies and reported that Mo metal lost activity rapidly but produced about the same product distribution as iron. Most recently, Hou and Wise (*4*) have studied the kinetics of methane formation on MoS_2. They found a very low activation energy for the formation of methane (~7.4 kcal/mol) and the dependence of the rate on reactant gas pressures to be

$$r_{CH_4} = kP_{CO}^{+1}P_{H_2}^{+0.5}.$$

This pressure dependence is unusual since the rate of CO hydrogenation is usu-ally of negative order with respect to CO pressure. The purpose of this study is to explore the catalytic activity of Mo for the CO/H_2 reaction. By using small-area (~1 cm²) single crystals of (100) orientation and polycrystalline foils we were able to determine the structure sensitivity of the reaction. Our low-pressure/high-pressure apparatus permits surface analysis by Auger electron spectroscopy before and after experiments. By adding potassium or sulfur in submonolayer quantities to the surface we were able to study the influence of these additives on the rates of formation of the products and thus, the product distribution.

The reaction produced mostly methane, ethene, and propene. We found positive pressure dependencies of the reaction rate on CO and H_2:

$$r_{CH_4} = kP_{CO}^{+0.32}P_{H_2}^{+1.0}.$$

This points to a reaction mechanism that is different from that found for CO hydrogenation on many other transition metals (Ni, Fe, Ru). The reaction proved to be structure insensitive under our conditions (pressure range 1–10 atm, temperature range

250–400°C). Both K and S, when added in submonolayer quantities, increased the olefin-to-paraffin ratio.

EXPERIMENTAL

All the experiments were carried out in an ultrahigh vacuum (UHV)/high-pressure apparatus designed for combined UHV surface analysis and high-pressure reaction studies using small-surface-area catalyst samples. This chamber is equipped with four-grid electron optics for LEED and AES, Ar$^+$ ion sputtering gun for crystal cleaning, a quadrupole mass spectrometer, and a retractable internal isolation cell that constitutes part of a microbatch reactor operating in the pressure range 10^{-2}–20 atm. The reaction cell and the external recirculation loop were connected to an isolable pressure gauge, a magnetically driven micropump for reaction gas circulation, and a gas chromatograph sampling valve. Hydrocarbon product formation was monitored with a HP5793 gas chromatograph equipped with a 12-ft. × ⅛-in. Poropak N column and a flame ionization detector.

The molybdenum single crystals used were obtained from the Materials Research Corporation and were cut and polished to within ±1° of the (100) face. The crystal was spot-welded to a rotatable manipulator using a series of Ta and Cu supports, that enabled the crystal to be resistively heated to ~1900 K without significant heating of any other part of the chamber. Both crystal faces (front and back) were cleaned by repeated oxygen treatment and annealing until no K, S, C, or O were detected by AES.

For potassium-doping studies coverages were estimated using the relative Auger sensitivities published in the Phi "Handbook of Auger Electron Spectroscopy," this approximation of the surface coverage is reasonable only for low coverages. Potassium was deposited under vacuum from a "SAES getters" potassium source mounted 2 cm from the sample. Oxygen coverages were determined by AES and LEED as described previously (5). Sulfur

coverages were determined by AES and LEED (for $\theta_s \geq 0.33$) as described previously (6). Research-purity H$_2$ (Matheson grade >99.9995% atomic purity) was passed through a stainless-steel coil in liquid nitrogen before use. Research-purity carbon monoxide (Matheson Grade >99.99% atomic purity) was passed through a molecular sieve trap in a dry ice/acetone bath prior to use.

In order to perform high-pressure experiments the reaction cell was raised, enclosing the clean or potassium-covered single crystal or polycrystalline foil catalyst within the high-pressure loop. The loop was then pressurized with either CO or H$_2$, and the circulation pump started. The second gas was then introduced into the loop over a period of ~3 min. The reaction rate was independent of the order in which the reactant gases were supplied. The gases were then mixed for 10 min and an initial sample was analyzed by gas chromatography. At this point the sample was heated to the desired reaction temperature. The reaction temperature was continuously regulated to within ±2 K using a precision temperature controller and a platinum/platinum 10% rhodium thermocouple spot-welded to one face of the sample. The temperature calibration was carefully checked using an isobutane–isobutene equilibrium mixture, as explained in detail previously (7).

Product formation was followed by gas chromatography. Initial reaction rates were determined graphically from the initial slopes of product accumulation curves as a function of time and were reproducible to within ±5%. Blank experiments performed on Mo covered with graphitic carbon, formed by heating the crystal in a hydrocarbon atmosphere at 600°C, showed only a low level of catalytic activity. For example, at 450°C the activity of the carbon-covered surface was less than 10% of the activity measured using clean Mo at the lowest reaction temperature, 150°C, used in this study.
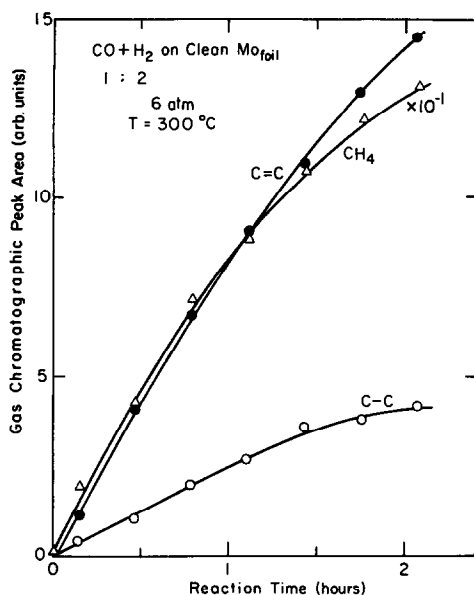
After completion of the high-pressure re-

FIG. 1. Product accumulation versus reaction time curves in closed-loop, batch reactor. The plot shows major products from CO + H$_2$ (1 : 2) at 6 atm of total pressure and a clean Mo$_{foil}$ catalyst temperature of 300°C.

action, the crystal was cooled to room temperature, the loop evacuated to less than 10^{-3} Torr using a mechanical pump and a liquid-nitrogen-trapped 2-in. oil diffusion pump, and the cell opened to expose the sample to UHV. The resulting surface was examined by AES, and in the case of Mo(100), LEED.

RESULTS

The catalytic hydrogenation of carbon monoxide has been investigated on Mo(100) single crystals and polycrystalline Mo foils. Typical initial turnover frequencies for methane production were 0.11 at 300°C, CO/H$_2$ = 0.33, and 4700 Torr total pressure and 0.011 at 275°C, CO/H$_2$ = 0.20, and 1320 Torr total pressure. We have defined turnover frequencies (product molecules/atom · second) using the surface atomic density of Mo(100) (1.0 × 10^{15} Mo atoms/cm^2). No correction has been made for the fact that Mo polycrystalline foil is not composed entirely of the (100) face. Using this definition no differences in either

rates or product distributions have been observed between single crystal or polycrystalline surfaces. Thus the reaction does not appear to be structure sensitive. A characteristic product accumulation curve is shown in Fig. 1. The duration of the reaction varied from 30 min to 24 h but generally reactions were stopped after 4 h. Typical product distributions for the hydrogenation of CO are shown in Fig. 2. An interesting characteristic of the CO hydrogenation reaction on Mo is its high selectivity toward olefinic products under our low conversion (≦1%) conditions. At a CO/H$_2$ ratio of ½, the rate of formation of ethene is four to six times greater than that of ethane. Of the products containing three carbon atoms, propene is observed almost exclusively.

The activation energy for the methanation reaction was determined by varying the temperature while holding the total pressure and reactant gas composition constant. On Mo it was found to be 24 ± 1 kcal/mol (see Fig. 3) similar to that found on Ni, Rh, Ru, and Fe (8–10). Similarly, the activation energy for ethane production was found to be 23 ± 1 kcal/mol (Fig. 4). The dependence of the methanation rate on the pressures of the reactant gases was determined by varying the partial pressure of
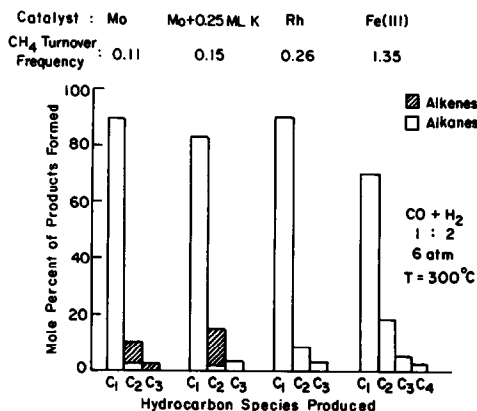

FIG. 2. Product distributions from CO hydrogenation over four different catalysts. The distributions for Rh and Fe(111) are taken from Refs. (8, 10), respectively.
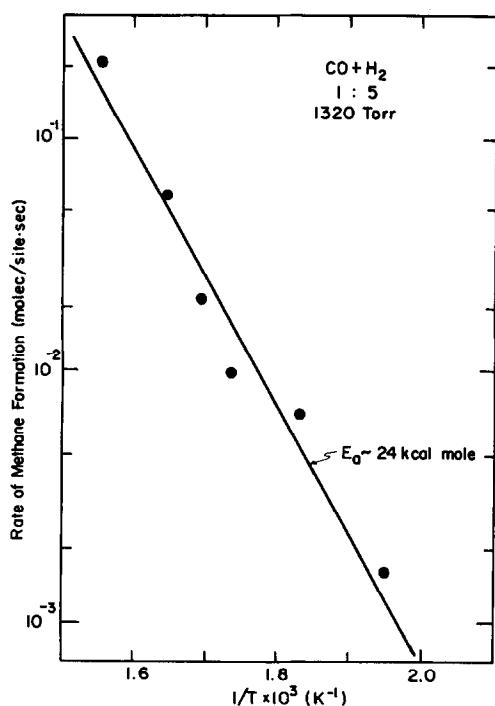
FIG. 3. Arrhenius plot for the initial rate of formation of methane vs inverse temperature (CO + H_2, 1:2, 6 atm). The plot gives 24 kcal/mol as the activation energy for methane production over Mo(100) single-crystal catalysts.

phitic carbon on the surface. When the surface was completely covered by graphitic carbon, as determined by the lineshape of the C_{1s} peak of the Auger electron spectrum (see Fig. 6), the rate of methane formation was less than 3% that of the clean metal catalyst under identical conditions (CO + H_2, 1:2, 6 atm, 350°C). In other experiments, reactions were stopped before deactivation of the catalyst surface took place and in these cases submonolayer amounts of carbidic carbon were detected by AES on the surface (see Fig. 6b). Auger electron spectra taken after the surface was deactivated during the hydrogenation reaction were also studied. In these cases the lineshape of the C_{1s} peak signifies graphitic carbon on the surface (see Fig. 6c). These studies indicate that the "active" surface is covered by a carbidic carbon species and the reaction is poisoned as the carbidic species is converted to graphitic carbon on the

each reactant gas while maintaining a constant total pressure and temperature, using nitrogen or argon as a buffer gas. The observed rate law for methanation (see Fig. 5) is given by

$$r_{CH_4} = kP_{CO}^{+0.32}P_{H_2}^{+1.0}.$$

In an attempt to produce longer-chain ($\geq C_3$) hydrocarbons via secondary reactions, ethene was added to the reactant gas mixture. The primary result of this addition was the hydrogenation of ethene to ethane, while no production of longer-chain hydrocarbons was observed. Thus, it appears that the propene produced is not the result of ethene reacting with CH_x fragments on the surface.

Deactivation of the surface was observed when the catalysts were pretreated by dosing with cyclohexene at 600°C forming gra-
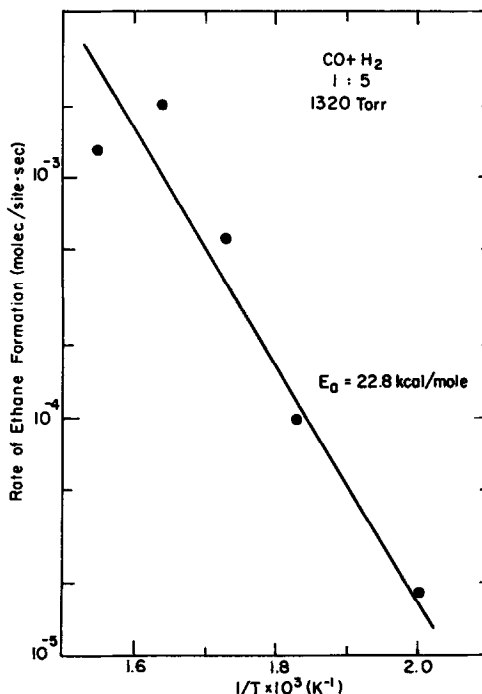

FIG. 4. Arrhenius plot for the initial rate of formation of ethane versus inverse temperature over Mo(100) single-crystal catalysts.
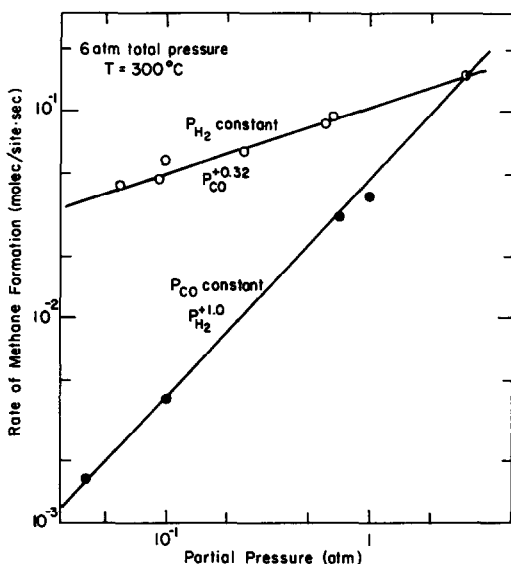
FIG. 5. Rate of formation of ethane versus the partial pressure of each reactant at a constant total pressure (constant H_2 pressure of 3 atm for determination of CO dependence and constant CO pressure of 3 atm for determination of H_2 pressure dependence). The resulting rate expression has the form

$$r_{CH_4} = KP_{CO}^{+0.32}P_{H_2}^{+1.0}.$$

surface. The rate of poisoning is determined by the ratio of CO to H_2 in the reaction mixture and by reaction temperature (lower CO : H_2 ratios and lower temperatures prolong the active catalysts lifetime).

Studies were also performed to determine the effect of alkali doping on the catalytic activity and selectivity. Figure 7 shows the reaction rate as a function of potassium coverage, for CO/H_2 = ½ at a total pressure of 6 atm and a temperature of 300°C. For low coverages of potassium (θ_K ~ 0.15 ML) an overall rate enhancement was observed on Mo$_{foil}$ samples. In addition, the product distribution shifted toward olefinic products. We see a factor-of-4 increase in the rate of formation of ethene while the rate of formation of methane and ethane remain virtually unchanged. At higher potassium coverages the total activity declines, signifying that the active sites for the reaction were partially blocked by over ~0.25 ML of K.

During the course of some of the reactions the surface was inadvertently contaminated by up to 0.5 ML of sulfur, as detected by AES after the reaction. In these circumstances it was noted that for a sulfur coverage of ~0.25 ML the rate of methane formation was attenuated by a factor of ~5 while the alkene production rate remained essentially unchanged relative to those rates observed on the clean Mo surface (see Fig. 8).

DISCUSSION

Under our conditions for CO hydrogenation, Mo(100) crystals and Mo polycrystalline foil produced primarily methane, ethene, and propene. This is unusual when compared to the product distribution over other transition metals that produce either
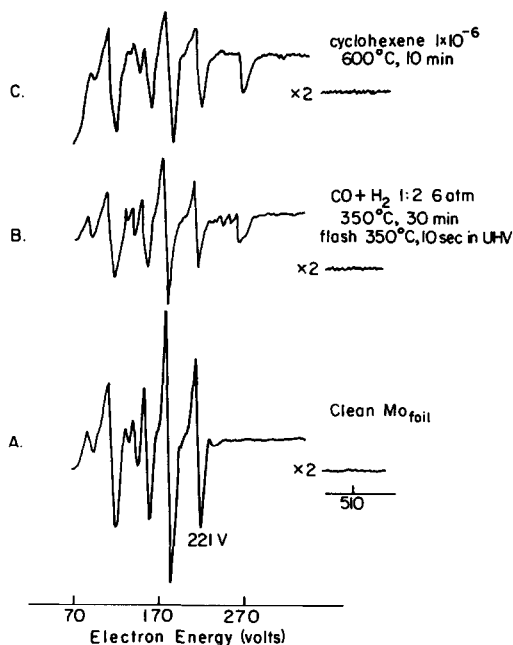

FIG. 6. Auger electron spectra of molybdenum foil showing the difference between carbidic and graphitic carbon on the surface. (A) AES of clean Mo$_{foil}$ after argon ion sputtering, oxygen treating (5 × 10^{-7} Torr O_2, 1000°C), and annealing at 1600°C for 3 min. (B) AES of Mo$_{foil}$ after running the hydrogenation of CO (CO + H_2, 1:2, 6 atm, 350°C) for 30 min, showing the formation of carbidic carbon on the surface. (C) AES of Mo$_{foil}$ after forming a graphitic overlayer on the surface with cyclohexene. Similar spectra were obtained after the catalyst was poisoned during a reaction.
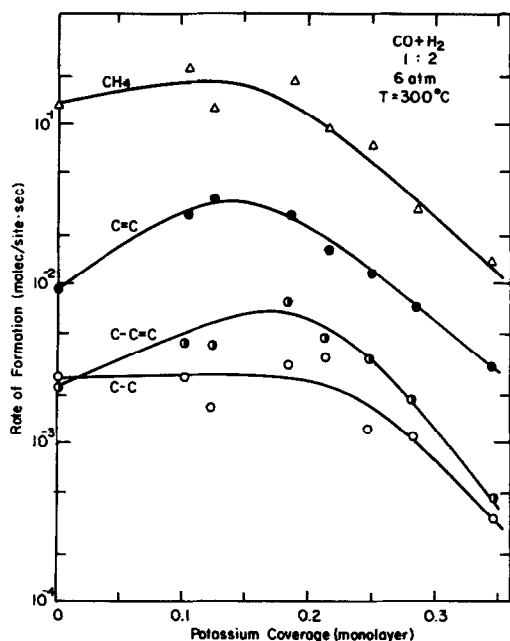
FIG. 7. A plot of the rates of product formation vs potassium coverage, showing the increase in the rate of alkene formation relative to the rate of alkane formation. This is due to an increase in the amount of dissociated CO on the surface as potassium is added to the surface (see Discussion).

Fe, Ru, and Co (9, 10). Thus, on Mo the adsorption of CO does not inhibit the hydrogenation rate as it does on other transition metals. One explanation for the observed positive-order pressure dependence for CO is that the high carbon levels observed under typical reaction conditions strongly weaken the bonding of CO to the surface, so that the rate-limiting step of the reaction is the formation of "active" or carbidic carbon by CO dissociation. With this model an increase in the CO partial pressure results in an increase in the surface coverage of active carbon and thus to an increase in the concentration of the reaction limiting species. The reaction proceeds through the same intermediate as is assumed for other Fischer–Tropsch catalysts and therefore the activation energy is similar. This mechanism could perhaps be verified by the absence of a deuterium isotope
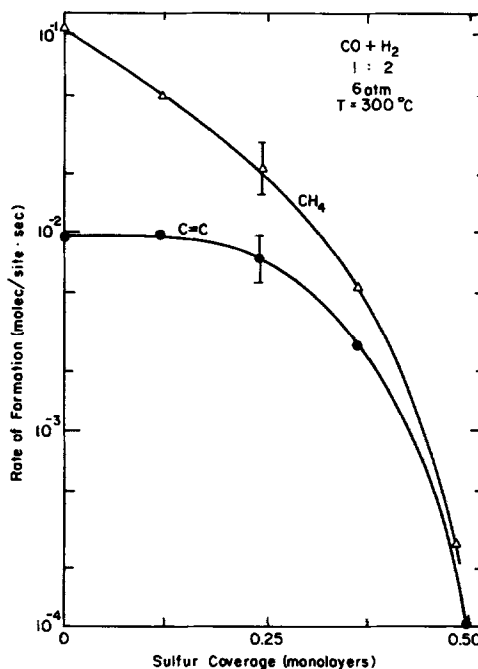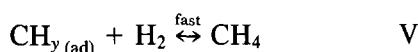
solely methane (Ni) or a distribution of higher-molecular-weight paraffin products (Fe, Ru, Co) that form by a chain growth mechanism (9–13). Only Rh metal foils produce C_1–C_3 hydrocarbons exclusively under these experimental conditions.

The selectivity of the reaction on Mo showed a high proportion of olefinic products. This indicates that Mo is a poor hydrogenation catalyst. The hydrogenation of carbon monoxide on Mo produces less than 1% of hydrocarbons with more than three carbon atoms. This, and the high alkene-to-alkane ratio, leads us to conclude that the rates of carbon–carbon and carbon–hydrogen bond formation reactions are slow relative to the desorption rates of small hydrocarbons on Mo.

The positive power of rate dependence on the pressure of CO is unusual since the methanation rate has a negative-order dependence on CO partial pressure over Ni,
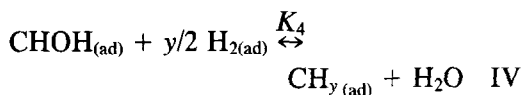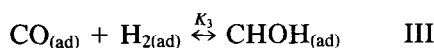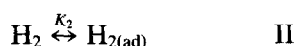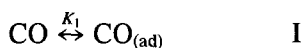

FIG. 8. Rates of product formation vs sulfur coverage on molybdenum foils, showing an enhancement in the rate of production of alkenes relative to the rate of production of alkanes. This is due to a decrease in the rate of hydrogenation as sulfur is added to the surface (see Discussion).

effect. Another explanation for this observation can be made by proposing a mechanism similar to that suggested by Sinfelt (14) and later modified by Vannice (15). In terms of this model the rate-determining step is the final hydrogenation of the CO–H₂ surface complex to rupture the C–O bond and all steps preceding it are in quasiequilibrium. The following set of elementary steps was proposed.

$$CO \overset{K_1}{\leftrightarrow} CO_{(ad)} \qquad I$$

$$H_2 \overset{K_2}{\leftrightarrow} H_{2(ad)} \qquad II$$

$$CO_{(ad)} + H_{2(ad)} \overset{K_3}{\leftrightarrow} CHOH_{(ad)} \qquad III$$

$$CHOH_{(ad)} + y/2\ H_{2(ad)} \overset{K_4}{\leftrightarrow}$$
$$CH_{y\ (ad)} + H_2O \quad IV$$

$$CH_{y\ (ad)} + H_2 \overset{fast}{\leftrightarrow} CH_4 \qquad V$$

If the surface is covered predominately by a strongly adsorbed CH_xOH species, whose surface coverage can be approximately by

$$\theta_{CHOH} = \frac{KP_{CO}P_{H_2}}{1 + KP_{CO}P_{H_2}} \sim (KP_{CO}P_{H_2})^N.$$

The sites remaining for hydrogen adsorption will be

$$1 - \theta_C = \theta \sim (KP_{CO}P_{H_2})^{-1}$$

and the fraction of the total surface covered by hydrogen will be

$$\theta_{H_2} = \frac{\theta K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2}} \simeq \theta K_{H_2}P_{H_2}$$

Then for the case where hydrogen is weakly adsorbed $K_{H_2} \ll 1$ and the rate of methanation is

$$r_{CH_4} = K\theta_C\theta_{H_2}^{y/2}$$

and upon substituting for the values of θ_C and θ_{H_2} we obtain an equation of the form

$$r_{CH_4} = KP_{CO}^{N-y/2}P_{H_2}^N.$$

Then for our case $N = 1$ and $y = 1$ would lead to a rate expression of the form

$$r_{CH_4} = KP_{CO}^{+0.5}P_{H_2}^{+1.0}.$$

It should be remembered that this mechanism for CO hydrogenation was first proposed in detail by Storch in 1948 (16) and later extended by Kummer and Emmett in 1953 (17).

It should be noted, however, that in spite of the different reaction mechanism that is proposed here, based on the unusual CO partial pressure dependence of the rate, the activation energy for methane formation is 24 kcal/mol, very similar to that found on other transition metals. In fact, the similar activation energy for ethane formation indicates that this hydrocarbon is formed by a mechanism similar to that for methane.

The production of ethene or propene can occur by the carbonylation of CH_x or C_2H_x fragments and their subsequent hydrogenation and dehydration by reaction steps similar to those proposed for methane formation. It should be noted that carbonylation is usually the chain-terminating step in CO hydrogenation as was shown for rhodium compound catalysts recently. To test this possibility ethene was added to the reaction mixture in the hope that propene or other higher-molecular-weight hydrocarbons would be produced. However, we found the ethene was either hydrogenated to ethane or did not react. This observation leads us to conclude that carbonylation is either a slow process or does not occur under our reaction conditions.

The hydrogenation of carbon monoxide over Mo surfaces is structure insensitive under our reaction conditions. This is indicated by the fact that rates and selectivities over foils and single crystal surfaces are similar. The structure insensitivity of most Fischer–Tropsch catalysts has been used to support the model that the reaction takes place on top of a carbidic overlayer on Fe, Ru, and Co.

Our studies on carbon coverage and its relation to a catalyst deactivation revealed that the reaction probably takes place on top of a carbidic overlayer. This overlayer

will deactivate by forming graphite on the surface and block the reaction sites. We found that with higher temperatures or higher partial pressures of carbon monoxide the rate of this deactivation process increased.

In an attempt to study the catalytic activity of molybdenum oxide we produced a surface layer of MoO_2 using the procedure described by Zhang et al. (5). Reactions performed over these surfaces exhibited the same rates and product distributions as those on clean surfaces. Auger spectra taken after the reaction indicate that the surface was reduced rapidly during the hydrogenation, suggesting that again the observed reaction takes place on a carbidic overlayer on the metallic surface.

Alkali doping of many metal surfaces facilitates carbon monoxide dissociation into carbon and oxygen (18, 19). It has been proposed that this is caused by lowering the dipole component of the work function at the surface thereby increasing back-donation of metal electrons into the CO $2\pi^*$ antibonding orbital (18). At reaction temperatures this accelerates the dissociation of CO, leading to higher coverages of carbon and oxygen on the surface. Assuming that hydrogenation is the rate-limiting step in the production of saturated hydrocarbons, K doping of the surface will increase the relative rate of production of unsaturated hydrocarbons (20, 21), as we have observed. Our observation of the K promotion effect differs from the work of Bridgewater et al. (22) on supported Mo catalysts. Under reaction conditions similar to ours Bridgewater et al. found that doping of Mo catalysts with K to 17 at.% results in a 20-fold reduction in activity. It is possible that this discrepancy is caused by the segregation of potassium to the surface of the supported catalyst. This might be expected given the relative surface free energies of K_s (397 dyn/cm) (18) and Mo_s (1900 dyn/cm) (23). Since Bridgewater et al. give data for one particle size and do not use a surface-sensitive spectroscopic technique

such as AES, it is not possible to determine the surface concentration of K on their catalyst.

The addition of S to the surface increases the olefin-to-paraffin ratio. We can rationalize our observation in terms of a selective blocking of H_2 adsorption sites. The work of Clarke (24) had shown that CO adsorption on the Mo(100) surface is blocked completely at sulfur coverages of 0.5 ML. Other work in this laboratory shows that H_2 adsorption is effectively blocked by ordered S overlayers at coverages as low as 0.25 ML (25, 26). If sulfur preferentially inhibits H_2 adsorption then its presence on the Mo surface will result in a decreased hydrogen-to-carbon ratio on the surface. Although there will be an overall decrease in reaction rate, the olefin-to-paraffin ratio should increase, as observed.

CONCLUSIONS

The hydrogenation of CO on Mo surfaces in the pressure range 1–10 atm and temperature range 250–400°C primarily produces methane, ethene, and propene. The reaction rate exhibits positive order in CO pressure for CH_4 formation unlike other methanation catalysts. The reaction also produces a large fraction of ethene and propene instead of saturated hydrocarbons as observed for other transition metal catalysts (Fe, Re). The addition of K to the surface, at low coverages causes an increase in the overall rate and a shift in selectivity toward unsaturated products. This has been explained in terms of an electronic effect by which K induces back-donation of electrons into the CO $2\pi^*$ orbital increasing the amount on CO dissociation on the surface. The addition of S to the surface, on the other hand, causes a decrease in the overall rate but again an increase in the fraction of unsaturated products. This has been explained in terms of selective adsorption site blocking, preferentially reducing the amount of hydrogen on the surface.

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