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October 1984

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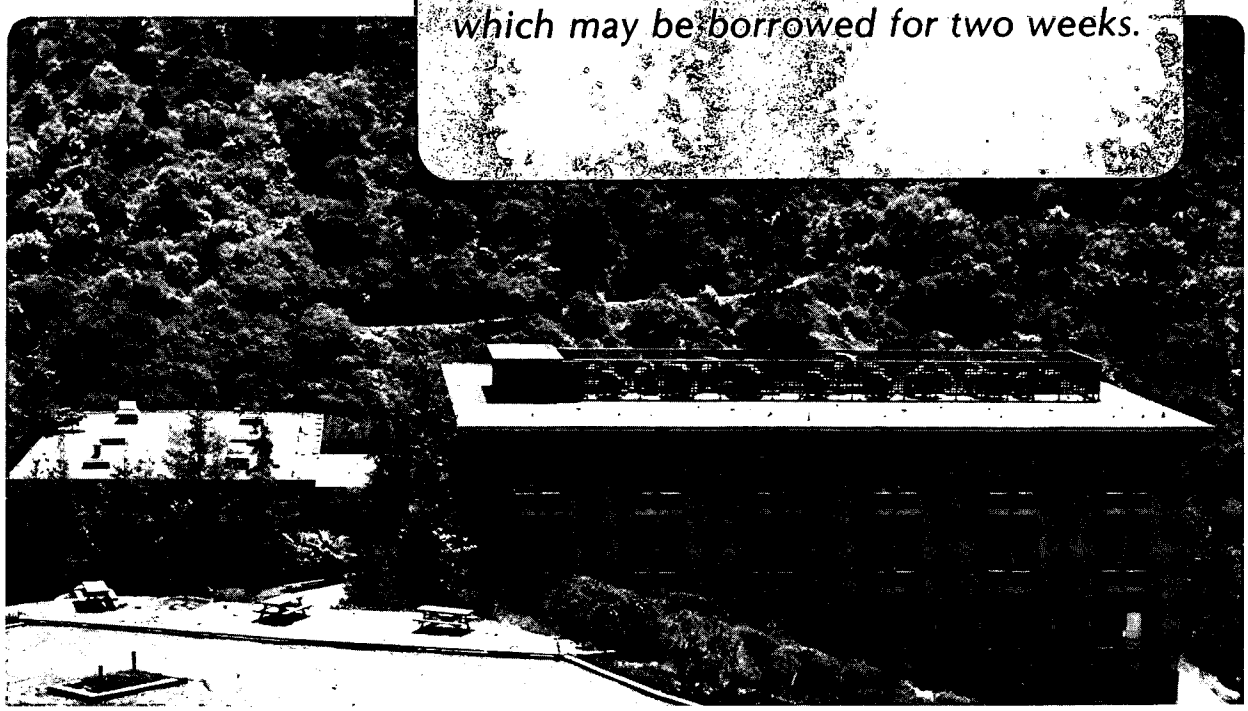

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HYDROGENATION OF CARBON MONOXIDE ON Mo(100) SINGLE CRYSTALS AND POLYCRYSTALLINE FOILS

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ABSTRACT

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 $r_{CH_4} = K P_{CO}^{+.32\pm.05} P_{H_2}^{+1.0\pm0.1}$. 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 as much as a factor of 5.

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[1,2,3,4]. 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 be

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

This pressure dependence is unusual since the rate of CO hydrogenation is usually 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 cm^2) 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 the 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

$$r_{CH_4} = k\, P_{CO}^{+0.32} P_{H_2}^{+1.0} .$$

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 (1-10atm), temperature range (250-400^{o}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 10^{-2} - 20 atm pressure range. The reaction cell and the external recirculation loop were connected to an isolatable pressure gauge, a magnetically driven micropump for reaction gas circulation and a gas chromatograph sampling valve. Hydrocarbon product formation was monitored with HP5793 gas chromatograph equipped with a 12' x 1/8" 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 $\pm 1^{o}$ of the (100) face. The crystal was spotwelded to a rotatable manipulator using a series of Ta and Cu supports, that enabled the crystal to be resistively heated to ~1900K 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 calculated using the relative Auger sensitivities published in the Phi "Handbook of Auger Electron Spectroscopy". Potassium was deposited in 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 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 ± 2K using a precision temperature controller and a platinum/platinum 10% rhodium thermocouple spotwelded 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 a low level of catalytic activity, never higher than 10% of the activity measured using clean Mo at any given reaction temperature.

After completion of the high pressure reaction, 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" 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 = 0.02 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 Figure 1. The duration of the reaction varied from 30 min. to 24 hours, but in general reactions were stopped after 4 hours. Typical product distribtutions for the hydrogenation of CO are shown in Figure 2. An interesting characteristic of the CO hydrogenation reaction on Mo is its high selectivity towards olefinic products under our low conversion (≤ 1%) conditions. At a CO/H_2 ratio of 1/2 the rate of formation of ethene is 4-6 times greater than that of ethane. Of the three carbon containing products, propene is observed almost exclusively.

The activation energy for methanation on Mo was found to be 24 ± 1 kcal/mole (see Figure 3) similar to that found on Ni, Rh, Ru, and Fe[8,9,10]. The activation energy for ethene production was found to be 23 ± 1 kcal/mole (Figure 4). The dependence of the methanation rate on the pressures of the reactant gases was determined by varying the partial pressure of 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 Figure 5) is given by:

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

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. When the surface was completely covered by multi-layers of carbon, as determined by Auger electron spectroscopy (AES), the rate of methanation was no more than ~10% of the clean metal catalyst. In other experiments reactions could be stopped as deactivation was taking place and in these cases submonolayer amounts of carbon were detectable on the surface after flashing the sample up to reaction temperatures under UHV conditions and noting the production of methane. More studies of deactivation to quantify these observations are planned in the future.

Studies were performed to determine the effect of alkali doping on the catalytic activity and selectivity. Figure 6 shows the reaction rate as a function of potassium coverage, for $CO/H_2 = 1/2$ at a total pressure of 6 atm. and a temperature of 300°C. For low coverages of potassium ($\Theta_K \sim .15$ ML) a rate enhancement was observed on Mo_{foil} samples. In addition, the product distribution shifted towards 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 ~.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 Figure 7).

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 solely methane (Ni) or a distribution of higher molecular weight paraffin products (Fe, Ru, Co) that form by a chain growth mechanism.[9,10,11,12,13] 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 very few hydrocarbons longer 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 pressure is unusual as the methanation rate has a negative order dependence on CO partial pressure over Ni, 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. This may be explained by a mechanism similar to that proposed by Sinfelt[14] and later modified by Vannice.[15] In terms of this model the rate determining step is the final hydrogenation of the $CO-H_2$ surface complex to rupture the C-O bond and all steps proceeding it are in quasiequilibrium. The following set of elementary steps was proposed.

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

$$H_2 \overset{K_2}{\Leftrightarrow} H_2(ad) \qquad II$$

$$CO(ad) + H_2(ad) \overset{K_3}{\Leftrightarrow} CHOH(ad) \qquad III$$

$$CHOH(ad) + Y/2\ H_2(ad) \overset{K_4}{\Leftrightarrow} CHy(ad) + H_2O \qquad IV$$

$$CHy(ad) + H_2 \overset{fast}{\Leftrightarrow} CH_4 \qquad V$$

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

$$\Theta_{CHOH} = (K P_{CO} P_{H_2})^N,$$

and where hydrogen is relatively weakly adsorbed then the rate of formation of methane is given by

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

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

$$r_{CH_4} = K P_{CO}^{+.5} P_{H_2}^{+1.0}.$$

It should be remembered that this mechanism for CO hydrogenation was first proposed by Kummer and Emmett in 1953.[16,17]

It should be noted however that inspite 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/mole, 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 similar mechanism 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.

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 monoxde the rate of this deactivation process increased.

In an attempt to study the catalytic activity of molydenum 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 A.J. 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 atomic percent 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 dyne/cm[18] and Mo_s (1900 cyne /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 in 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 of 1-10 atm and temperature range of 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 selectvitiy towards unsaturated products. This has been explained in terms of an electronic effect by which K induces backdonation 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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FIGURE CAPTIONS

Figure 1 Product accumulation in closed loop, batch reactor.

Figure 2 Product distributions from CO hydrogenation over four different catalysts. The distributions for Rh and Fe(111) are taken from Refs. 8 and 10 respectively.

Figure 3 Arrhenius plot of CH_4 production rate vs. T^{-1}.

Figure 4 Arrhenius plot of C_2H_6 production rate vs. T^{-1}.

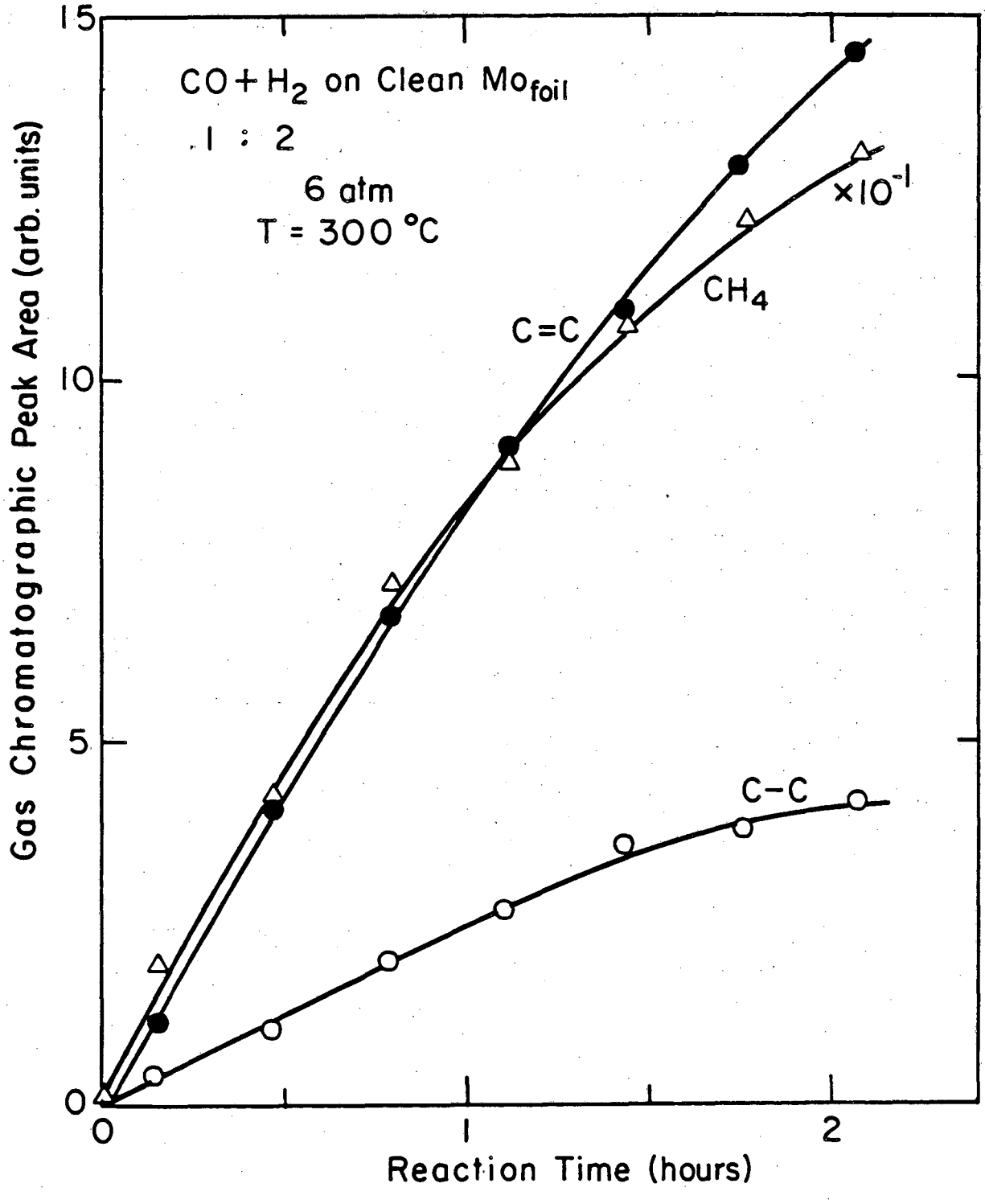
Figure 5 formation of CH_4 vs. partial pressure of each reactant. The resulting rate expression has the form

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

Figure 6 Rates of product formation vs. K coverage.

Figure 7 Rates of product formation vs. S coverage.

Fig. 1



XBL 849-3708

Fig. 2

$CO + H_2$
1 : 2
6 atm
T = 300°C

Catalyst :	Mo	Mo+0.15 ML K	Rh	Fe(III)
CH_4 Turnover Frequency :	0.11	0.15	0.26	1.35

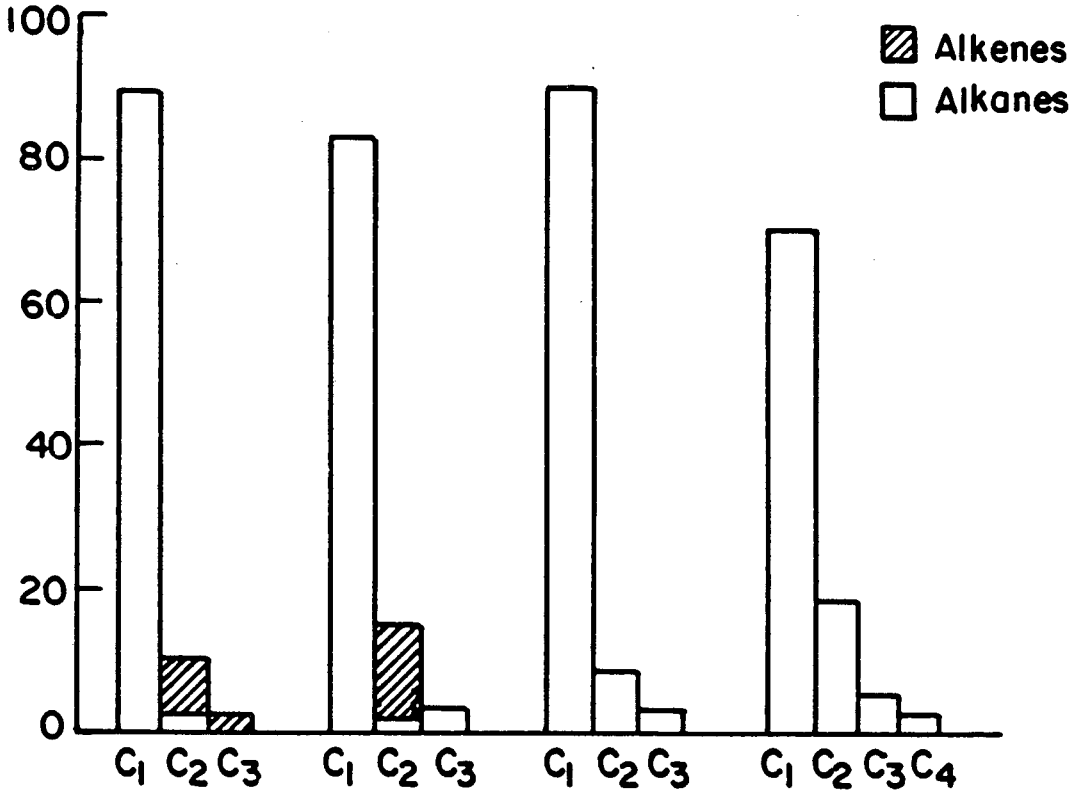


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Fig. 3

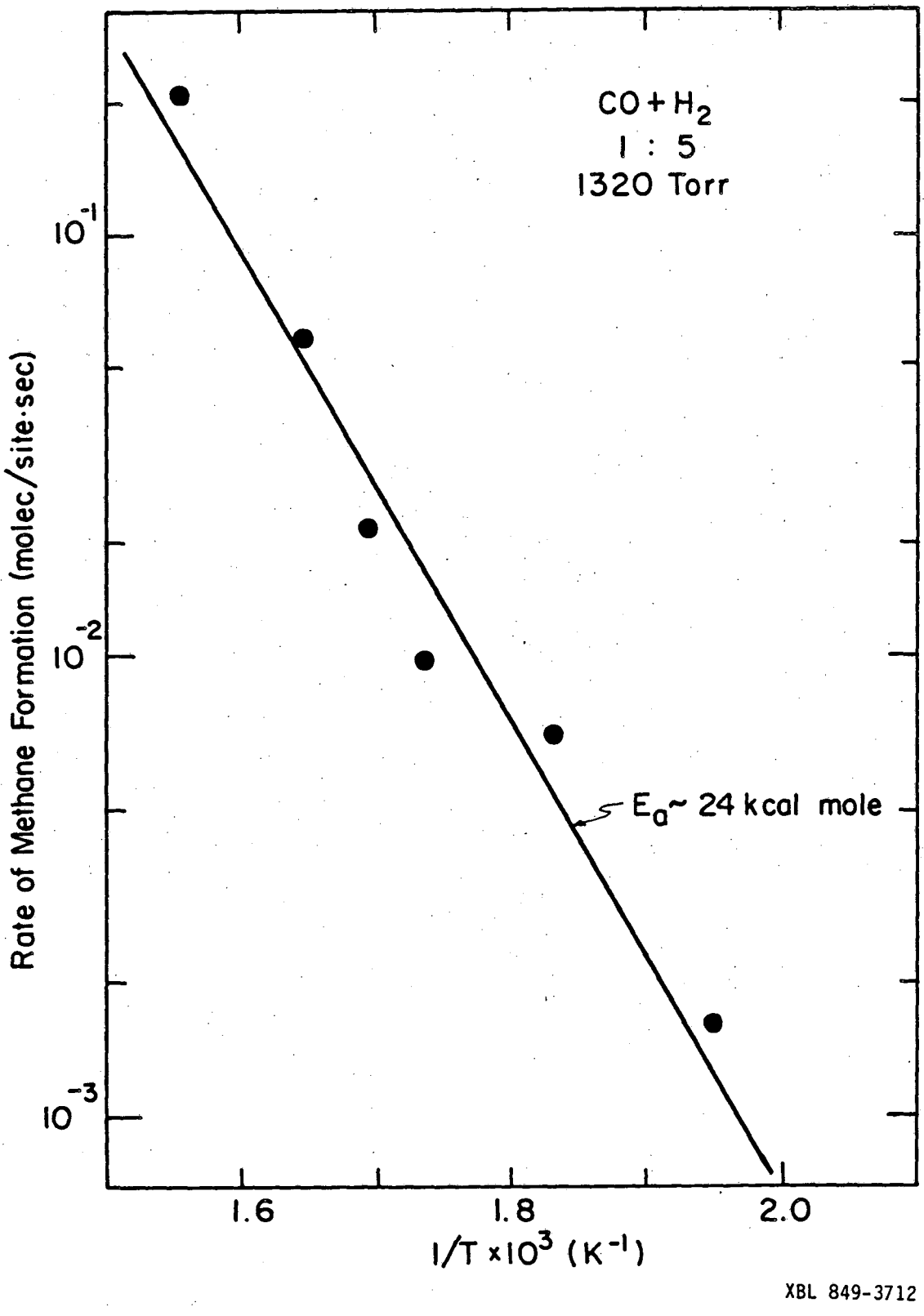
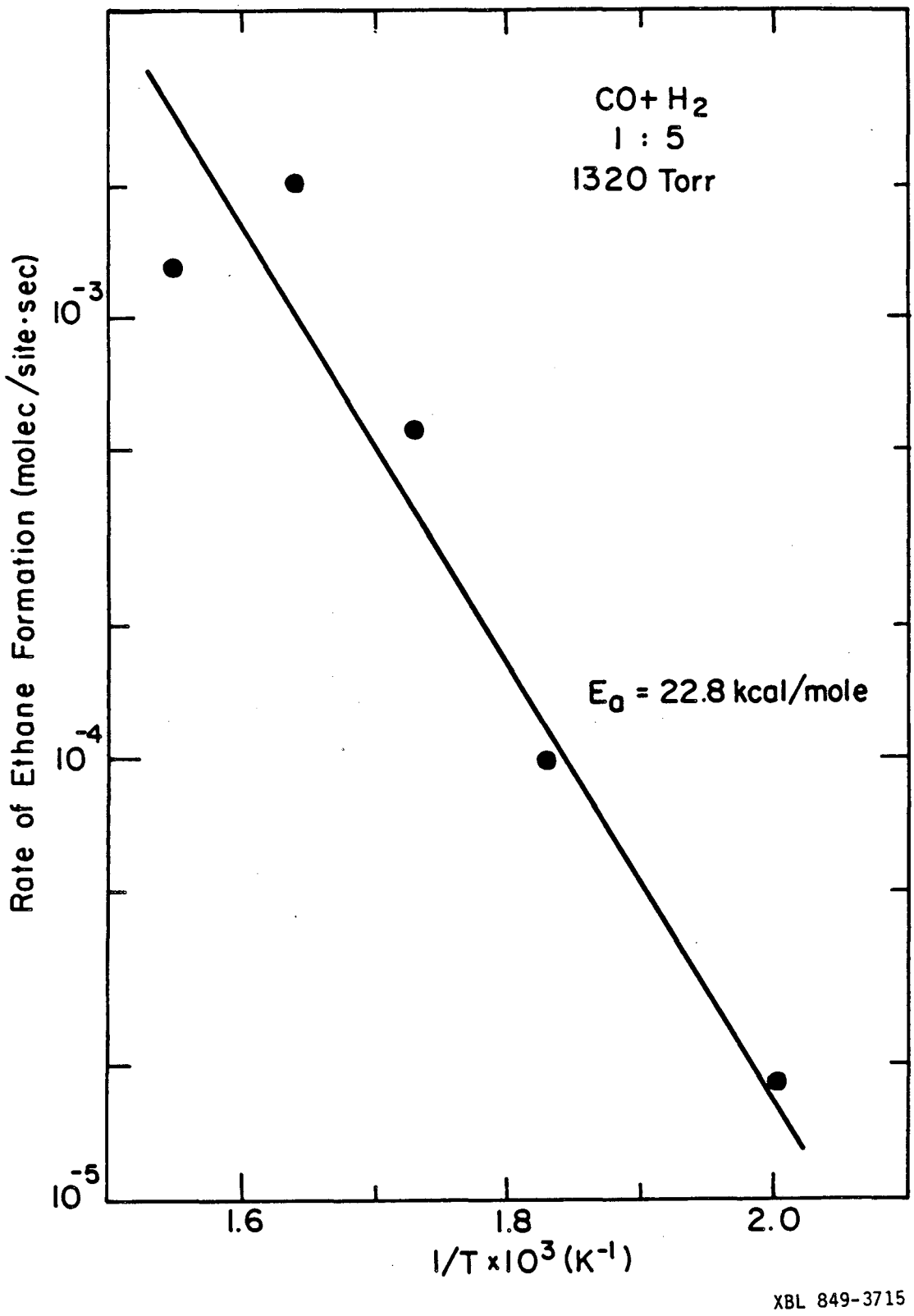
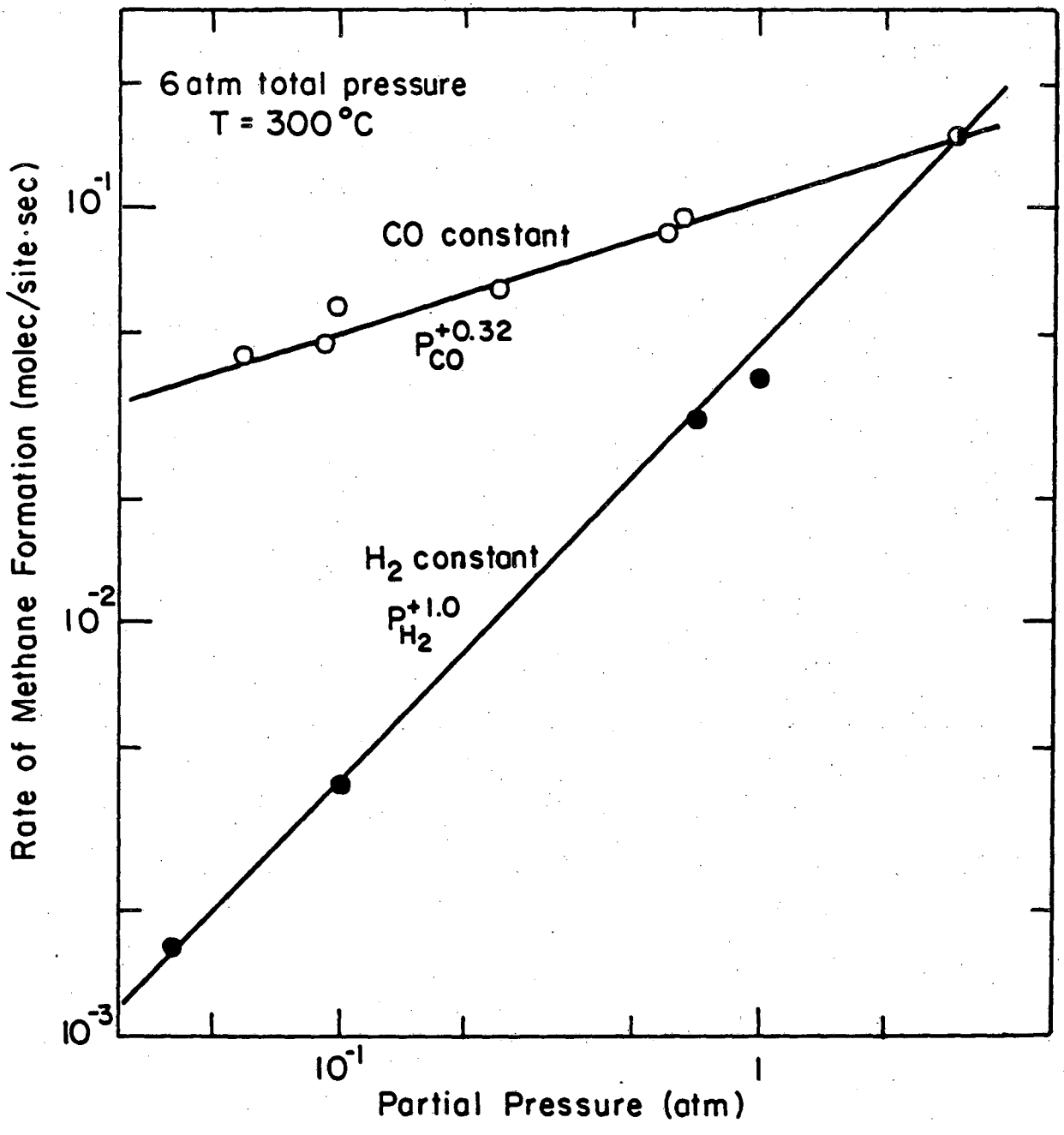

CO + H2
1 : 5
1320 Torr
Ea ~ 24 kcal mole
Rate of Methane Formation (molec/site·sec)
10-1
10-2
10-3
1.6
1.8
2.0
1/T x10^3 (K-1)
XBL 849-3712

Fig. 4



XBL 849-3715

Fig. 5



XBL 849-3713

Fig. 6

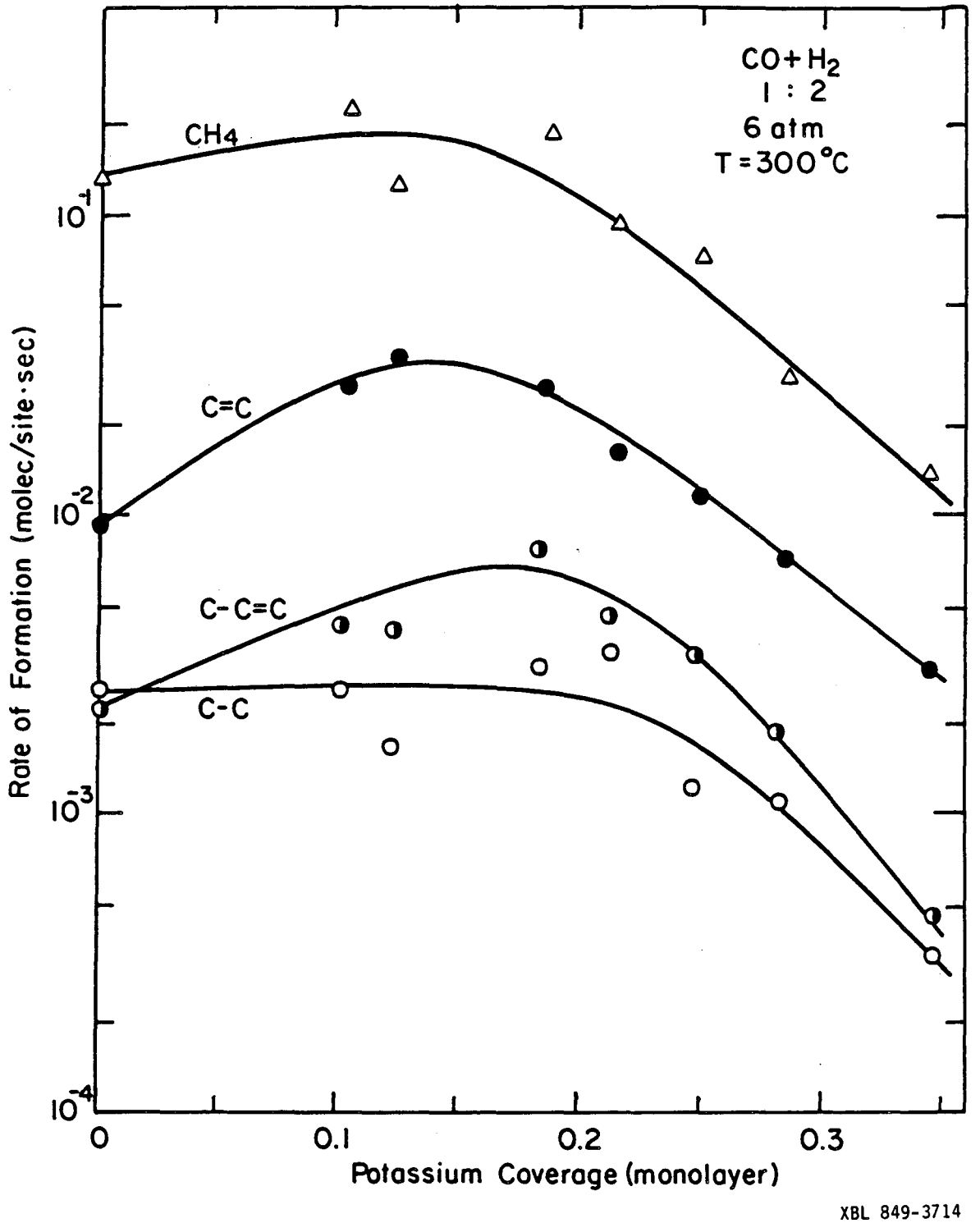
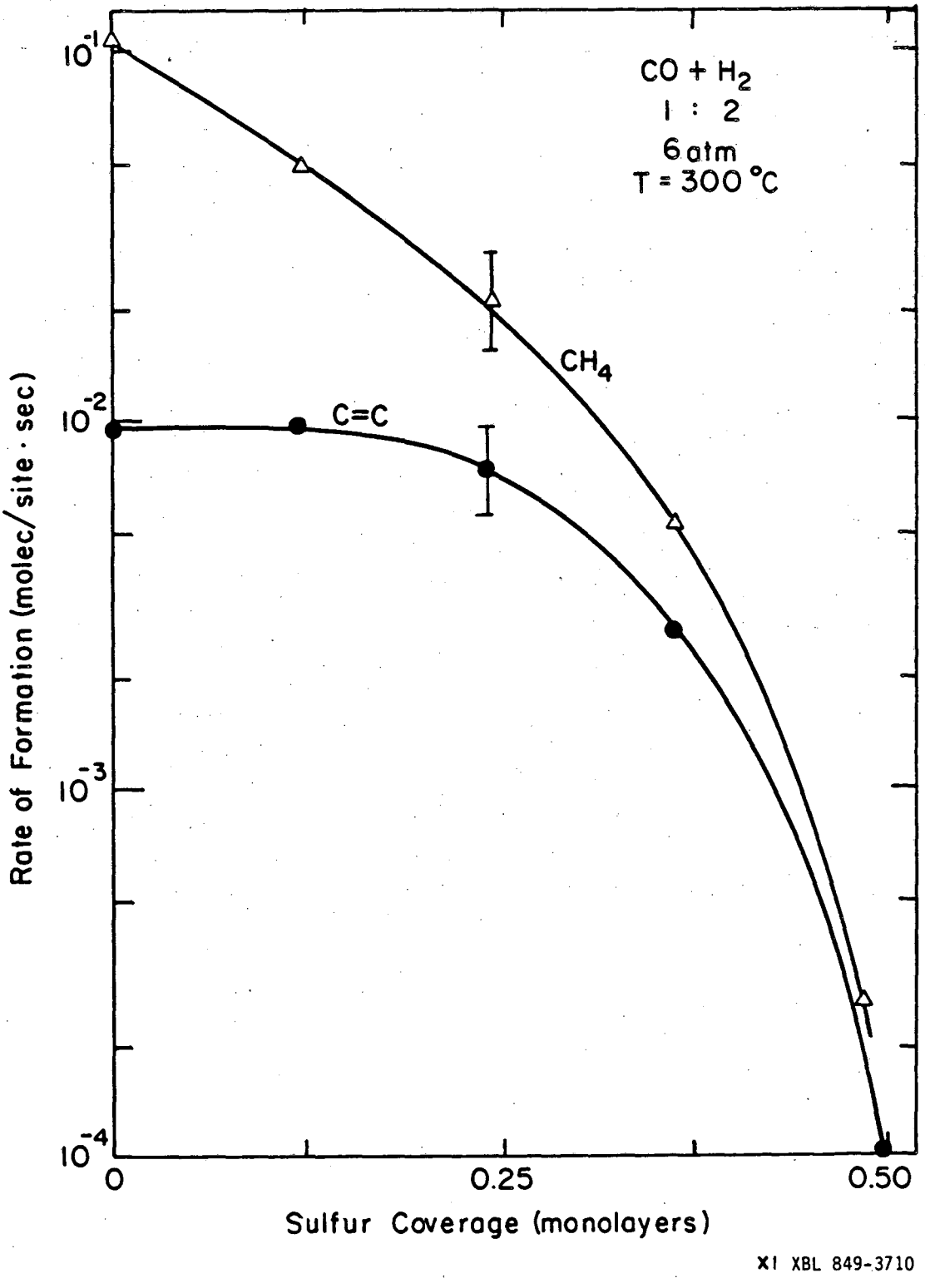

CO+H2
1 : 2
6 atm
T=300°C
CH4
C=C
C-C=C
C-C
Rate of Formation (molec/site·sec)
10-1
10-2
10-3
10-4
0
0.1
0.2
0.3
Potassium Coverage (monolayer)
XBL 849-3714

Fig. 7


CO + H2
1 : 2
6 atm
T = 300 °C
CH4
C=C
Rate of Formation (molec/site · sec)
10-1
10-2
10-3
10-4
0
0.25
0.50
Sulfur Coverage (monolayers)
X1 XBL 849-3710

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