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Studies of CO Desorption and Reaction with H_2 on Alumina-Supported Ru

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Abstract

The temperature programmed desorption (TPD) of CO and temperature programmed reaction (TPR) of chemisorbed CO in H_2 have been studied on a Ru/Al_2O_3 catalyst. Adsorption at 303°K occurs molecularly and leads to the observation of two peaks in the TPD spectrum. The activation energies associated with these peaks are 27 and 37 Kcal/mole. Upon heating above 415°K CO disproportionation takes place, forming CO_2 and carbon. The carbon deposited on the catalyst surface readily reacts with H_2 at 303°K to produce methane and ethane. These products are also formed during TPR of chemisorbed CO . The mechanism of CO disproportionation, the effect of surface carbon on the bonding of chemisorbed CO , and the reactions of chemisorbed CO with H_2 are discussed.

INTRODUCTION

Surface carbon formed by dissociation of chemisorbed CO has recently been shown to play an important role in Fischer-Tropsch synthesis over Ru catalysts. Rabo et al. (1) have reported that CO adsorption on a Ru/SiO_2 catalyst at 400°C is largely dissociative, resulting in disproportionation to CO_2 and Ru-C species. Hydrogenation of the carbon species at 23°C produces methane, ethane, and traces of propane. Under similar conditions molecularly adsorbed CO is totally unreactive. In a study of Fischer-Tropsch synthesis over a Ru/SiO_2 catalyst Ekerdt and Bell (2) have noted that the catalyst maintains a carbon reservoir several Ru monolayers in magnitude. A part of the carbon appears to be dissolved in the Ru but all of it readily reacts with H_2 to form methane, ethane, and propane. Since these products could be formed in the absence of chemisorbed CO , it was suggested that chain propagation in Fischer-Tropsch synthesis does not involve CO insertion but rather proceeds via addition of surface carbenes.

The present work was aimed at identifying the forms of CO present on Ru , the conditions under which CO disproportionation takes place, and the reactivity of the surface carbon formed. These studies were carried out on a Ru/Al_2O_3 catalyst using the techniques of temperature programmed desorption (TPD) and temperature programmed reaction (TPR). Results similar to those reported here have concurrently been obtained by McCarty et al. (3).

EXPERIMENTAL

Apparatus

The reactor used for these studies consisted of a 6 mm o.d. quartz tube with a 12 mm o.d. bulb-shaped midsection. A quartz fritted disk, used to support the catalyst, was fused into the midsection of the reactor. The reactor was heated by a small furnace made by winding nichrome wire around a 19 mm o.d. quartz tube. Current for the heater was supplied by a programmable power supply. This device allowed the reactor temperature to be maintained constant or to be raised at a rate of 0.03 to 1.0°K/sec. Feedback for the power supply was provided by a thermocouple located between the reactor and inside wall of the furnace. The catalyst temperature was recorded by a sheathed thermocouple positioned directly over the quartz disk supporting the catalyst.

The reactor inlet was connected to a gas manifold which could supply a continuous flow of a given gas or gas mixture. A gas injection valve was connected in series with the line feeding the reactor to permit injection of adsorbate pulses. The volume of each pulse was approximately 1.5 cm^3 at STP. The effluent from the reactor was analyzed by a UTI model 100 C mass spectrometer. A variable leak valve was used to introduce a constant leak of gas leaving the reactor into the vacuum chamber housing the mass spectrometer probe. During an experiment the leak valve was adjusted to maintain a constant pressure of 2.0×10^{-6} torr within the vacuum system. An ultimate pressure of 5×10^{-9} torr could be achieved with the leak valve closed.

Materials

A 5% Ru/Al_2O_3 catalyst was prepared by the incipient-wetness technique. Ruthenium trichloride (Orion Chemical Co.) was used as the source of Ru and Alon C (Cabot Corp.) was used as the support. The slurry of $RuCl_3$ on alumina was freeze dried and then reduced in flowing H_2 for 2.5 hrs at 673°K. The reduced catalyst was sieved to obtain particles smaller than 4.5 μm. The surface area of the catalyst was determined by H_2 chemisorption at 373°K (4). The equilibrium amount of H_2 adsorbed in the presence of 400 torr of H_2 was 71 μmoles/g of catalyst. Based upon this figure the catalyst dispersion was calculated to be 29%.

Hydrogen (99.999%) was passed through an Engelhard Deoxo unit to convert traces of O_2 to water and then through a bed of liquid nitrogen cooled molecular sieves to remove water. Helium (99.998%) was also purified using a liquid nitrogen trap filled with molecular sieves. Carbon monoxide (99.8%) was passed through a bed of potassium hydroxide pellets kept at dry ice temperature to remove CO_2 and metal carbonyls.

Experimental Procedures

A fresh 25 mg sample of the catalyst was used for each experiment. Following introduction of the sample into the reactor, air was eliminated from the flow system by a mechanical vacuum pump. The sample was then reduced in 1 atm of flowing H_2 at 773°C for 9 hrs or more. At the end of the reduction period, He was introduced to sweep away the H_2

and the sample was heated from 773°K to 973°K at a rate of 1°K/sec to desorb any adsorbed H_2. The sample was then cooled to the adsorption temperature in flowing He.

For TPD experiments, ten CO pulses were passed over the catalyst in a period of 5 min. This amount of contact was found to be sufficient to saturate the Ru catalyst at 303°K. Any CO_2 formed during adsorption was collected in a liquid nitrogen cold trap placed downstream from the reactor. The amount of CO_2 collected was subsequently measured by vaporizing the CO_2 into a flow of He and analyzing the stream with the mass spectrometer. Following CO adsorption, the catalyst was swept with He for 5 min at the adsorption temperature and finally cooled to 303°K in approximately 15 min. The He flow rate was then adjusted to 30 STP cm^3/min, and the catalyst was heated from 303°K to 973°K at 1°K/sec. During this period the concentrations of CO and CO_2 were monitored as a function of temperature.

The same reduction and adsorption procedures were used for the TPR of preadsorbed CO as were used for TPD. Following adsorption the catalyst was cooled to 303°K in flowing He. The He flow to the reactor was then curtailed and a 56 STP cm^3/min flow of H_2 was introduced. The amount of methane and ethane formed at 303°K was monitored. The catalyst was then heated in flowing H_2 at 1°K/sec. During this period the concentrations of methane and ethane in the H_2 stream were recorded as a function of temperature.

RESULTS

Temperature-Programmed Desorption of CO

A TPD spectrum of CO adsorbed to saturation coverage at 303°K is shown in Fig. 1a. Two distinct CO peaks are observed at 460 and 620°K and a high temperature shoulder can be seen on the second peak. In addition two CO_2 peaks are observed at 525 and 660°K. The presence of CO_2 indicates that the disproportionation of CO via the reaction $2CO \rightleftarrows C_s + CO_2$ occurs during desorption.

To test whether readsorption of CO had a significant effect on the TPD spectrum, a spectrum was taken using a He flow rate of 210 cm^3/min. This spectrum is shown in Fig. 1b. Comparison of the spectra in Figs 1a and 1b shows that while the spectra are qualitatively similar, the CO peaks shift to cover temperatures with increasing He flow rate. This observation clearly indicates that readsorption of CO does occur. In addition we see that the ratio of CO_2 to CO areas is smaller at the higher He flow rate.

To identify the temperature at which CO_2 is first formed, a CO/He stream containing 9% CO was passed over the catalyst while the temperature was raised from 303° to 973°K at 1°K/sec. The concentration of CO_2 appearing in the effluent stream as a function of temperature is shown in Fig. 2. Carbon dioxide formation is first noticed at about 415°K. The CO_2 concentration rises rapidly with temperature but reaches a maximum at about 740°K and subsequently declines. This pattern suggests that below 740°K the CO disproportionation is controlled by reaction kinetics but that at higher

temperatures reaction equilibrium controls the product composition. Such an interpretation is consistent with the fact that CO disproportionation is an exothermic process.

To establish the effects of temperature on the adsorption and desorption characteristics of CO , a series of experiments were conducted in which pulses of CO were passed over the catalyst, maintained at a fixed temperature. The formation of CO_2 was observed at temperatures of 423°K and above the amount of carbon deposited on the catalyst due to CO disproportionation is given in Table 1. This quantity is expressed as a fraction of the total amount of CO which can be adsorbed at 303°K. As the temperature increases above 423°K the amount of carbon deposited increases rapidly. However, even at 623°K, the fraction of sites available for CO adsorption, which are covered by carbon, is only 0.6%.

The influence of adsorption temperature on the TPD of CO is shown in Fig. 3. For adsorption at 423°K and above the only feature observed is the envelope of one or more high temperature peaks. The peak temperature associated with the envelope shifts to higher temperatures and the area under the envelope declines as the temperature of CO adsorption increases. The proportion of CO_2 to CO observed during TPD also decreases as the adsorption temperature increases.

Temperature-Programmed Reaction of CO with H_2

The reactivity of species produced by CO adsorption at different temperatures was examined by TPR and the results are shown in Fig. 4.

The spectra obtained for CO adsorption at 303 and 423°K are quite similar. The methane signal consists of two major features, a well defined peak at 400°K and a broad low intensity peak at about 500°K. A pair of overlapping peaks centered at 350 and 410°K are also observed for ethane. When the CO adsorption temperature is raised to 523°K several new features appear. The most striking is a very narrow spike of methane produced at 303°K. Small amounts of ethane are also produced at 303°K. As the temperature is raised three methane peaks are now observed -- a low temperature peak at around 350°K, an intermediate temperature peak at 460°K, and a high temperature peak at about 550°K. Two ethane peaks are again observed but the proportion of ethane to methane formed is larger than when CO is adsorbed at 303 or 423°K. Increasing the CO adsorption temperature to 623°K enhances the amount of methane produced at 303°K relative to that formed at higher temperatures. The remaining methane peaks are now observed at 350, 550, and 650°K. The ethane spectrum continues to show two peaks but the high temperature peak is now shifted to 500°K. The decrease in the overall amount of methane produced with increasing CO adsorption temperature reflects the decrease in the amount of CO adsorbed (see Fig. 3).

In view of the fact that carbon deposition occurs when CO is adsorbed at elevated temperatures, a comparison was made of the amounts of methane formed at 303°K with the amount of carbon deposited. The results are given in Table 2. Also listed in Table 2 is the fraction of the total methane formed occurring at 303°K. It is evident

that for CO adsorption at 523 and 623°K the amount of carbon deposited during adsorption and the amount of methane formed at 303°K parallel each other. It is also seen that the fraction of the methane formed at 303°K increases with increasing CO adsorption temperature, confirming the qualitative observations of Fig. 4.

DISCUSSION

The TPD spectra presented in Fig. 1 show two well defined peaks suggesting that CO desorption occurs from different states. The activation energies associated with the two peaks are listed in Table 3. These values were calculated on the assumption of first order kinetics and a desorption frequency factor of 10^{13} sec^{-1}. Peak temperatures determined from Fig. 1b were used to minimize the influence of CO readsorption. Also listed in Table 3 are activation energies for CO desorption from several surfaces of Ru single crystals (5-9). The activation energy for the low temperature peak observed in this work is 27 Kcal/mole and falls midway between the activation energies reported for CO desorption from molecular states in single crystal studies. The failure to observe two low temperature peaks may be due to the lower heating rate used in these experiments compared with those used for flash desorption from crystals. Thus it is possible that the low temperature peak seen in Fig. 1 is composed of two components.

The high temperature peak seen in Figs. 1 and 2 appears to be unique to desorption from supported Ru . A similar peak was not

observed in single crystal studies, even when the crystal was heated in CO for extended periods of time (7,9). However, Fuggle et al. (7) have reported that a small high temperature peak, referred to as β-CO, could be produced by electron bombardment of CO adsorbed on a Ru(001) surface. The activation energy for this peak, assuming first order kinetics, is given in Table 1. While UPS, XPS, and XAES observations indicated that the appearance of β-CO was accompanied by CO dissociation and that β-CO occupied two surface sites, the exact structure of β-CO could not be established. Since the desorption activations energies associated with β-CO and the high temperature peak of this study are comparable, it is possible that β-CO may have been formed under the conditions of this study.

The appearance of CO_2 during the desorption of CO and the passage of CO over the catalyst at elevated temperatures confirms the formation of carbon via the disproportionation of CO. This reaction does not seem to be restricted to supported Ru since Singh and Grenga (10) have reported carbon deposition on a polycrystalline Ru sphere exposed to 760 torr of CO at 823°K. At the same time, we note that neither CO_2 formation nor carbon deposition were observed in CO adsorption-desorption experiments carried out with Ru single crystals under vacuum conditions. These observations suggest that the partial pressure of CO over the catalyst is an important factor in determining whether or not carbon deposition and concurrent CO_2 formation occur.

The deposition of carbon on the surface of Ru can be explained in terms of the following reaction sequence

(1) $CO + S \rightleftarrows CO_s$

(2) $CO_s + S \rightleftarrows C_s + O_s$

(3) $CO + O_s \rightarrow CO_2 + S$.

The equilibrium for reaction 2 is undoubtedly unfavorable since no evidence for CO dissociation is observed on Ru single crystals, even when the surface coverage of CO is very high. Consistent with this McCarty (3) has estimated that reaction 2 is endothermic by about 21 Kcal/mole. To deposit carbon, reaction 3 must occur and thereby interfere with the reverse of reaction 2. If the concentration of CO in the gas phase is very low, such as is this case during desorption into a vacuum, CO_2 formation cannot occur. The formation of CO_2 via reaction 4 must of necessity also be too slow to contribute to CO_2 formation.

(4) $CO_s + O_s \rightarrow CO_2 + 2S$.

Additional evidence supporting the mechanism represented by reactions 1 through 3 appears in Figs. 1 and 3. In Fig. 1 it was observed that the amount of CO_2 produced depended on the He flow rate. The ratio of the amounts of CO_2 to CO desorbed was 0.15 for a He flow rate of 30 STP cm^3/min but dropped to 0.08 when the He flow rate was increased to 210 STP cm^3/min. Relatively less CO_2 was formed in

the run with the higher He flow rate because the concentration of CO in the gas phase was lower during this run. A similar explanation would account for the reduction in relative amount of CO_2 to CO with increasing CO adsorption temperature, observed in Fig. 3.

Carbon present on the catalyst surface might be expected to influence the strength of CO adsorption by donating electrons to increase the degree of back bonding between the carbon atom of an adsorbed CO molecule and Ru surface atoms. An increase in the degree of back bonding would weaken the C-O bond but strengthen the Ru-C bond. Evidence for this phenomenon was reported by Dalla Betta and Shelef (11) in an infrared study of CO on Ru/Al_2O_3. They observed that the presence of carbon on the Ru surface lowered the stretching frequency of the adsorbed CO, implying a weakening of the C-O bond. The strengthening of CO adsorption through the interaction of CO with surface carbon might explain the appearance of the high temperature peak seen in Figs. 1 and 3 and the upscale shift in the peak temperature as the CO adsorption temperature is increased.

The carbon deposited upon CO adsorption at temperatures above 423°K readily reacts at 303°K to form methane and ethane, the yield of these products increasing with the amount of carbon present. By contrast, chemisorbed CO is totally unreactive at 303°K but will react at higher temperatures. Whether molecularly adsorbed CO reacts via direct hydrogenation or via dissociation followed by hydrogenation of the carbon formed cannot be answered by the present experiments. The results recently reported by Ekerdt and Bell (2), however, strongly

support the latter mechanism and show that not only methane but also ethane and propane can be produced from carbon, in the absence of chemisorbed CO, at rates comparable to those observed during steady-state Fischer-Tropsch synthesis. Based upon this evidence we are led to suggest that the methane and ethane observed during TPR are formed via hydrogenation of surface carbon.

While the carbon formed during adsorption is very reactive, it appears to lose activity upon thermal aging, in a manner similar to that described by Wentrcek et al. (12) for a Ni catalyst. It was seen in Figs. 4 c and d that at CO adsorption temperatures of 523°K and 623°K a methane peak becomes apparent at 600 to 800°K. It is quite possible that the methane formed in this temperature range is due to the reaction of a fraction of the originally deposited carbon which had aged during the period of TPR. Some aging might also have occurred during the period of carbon deposition since we note in Table 3 that the ratio of the carbon deposited originally to the amount of methane formed at 303°K decreases when the CO adsorption temperature is increased from 523°K to 623°K.

Finally, several comments are in order concerning the removal of oxygen from the catalyst surface. When CO alone is present over the catalyst, oxygen, formed by CO dissociation, is removed by reaction 3. However, under the conditions of TPR oxygen removal by reaction 5 becomes more important.

$$(5) \quad O_s + H_2 \rightarrow H_2O + S.$$

This conclusion is based upon the work of Ekerdt and Bell (2) in which it was noted that reaction 5 should be more efficient than reaction 3

in removing surface oxygen. Consistent with this they observed that the amount of carbon deposited on the catalyst was an order of magnitude higher when CO and H_2 were contacted with the catalyst than when CO alone was used. It was also observed that under steady-state reaction conditions the only product containing oxygen was water.

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Table 1. Extent of carbon deposition by CO disproportionation

T_{ads} (°K)	θ_C*
303	-
423	1.4×10^{-4}
523	1.6×10^{-3}
623	6.1×10^{-3}

* Defined as the ratio of CO_2 formed during adsorption to CO adsorbed at 303°K

Table 2. Yields of Methane during TPR

T_{ads} (°K)	Total CH_4 (orb. units)	CH_4 (@ 303°K)/total CH_4	CH_4 (@ 303°K)/CO_2 (@ T_{ads})
303	1.00	0.0	-
423	0.82	0.0	-
523	0.27	0.10	1.94
623	0.20	0.21	0.46

Table 3. Activation energies for CO desorption

Catalyst	E_d(Kcal/mole)			Ref.
5% Ru/Al_2O_3		27	37	present study
Ru(100)	24.4	30.1	-	(5)
Ru(001)	23.5	28	-	(6)
Ru(001)	25	29	34-37	(7)
Ru(101)	25	28	-	(8)
Ru(110)	24-39		-	(9)

FIGURE CAPTIONS

Fig. 1 Effect of He flow rate on the TPD spectrum of CO

Fig. 2 Effect of temperature on the disproportionation of CO

Fig. 3 Effect of CO adsorption temperature on the TPD spectrum of CO

Fig. 4 Effect of CO adsorption temperature on the TPR spectrum of CO

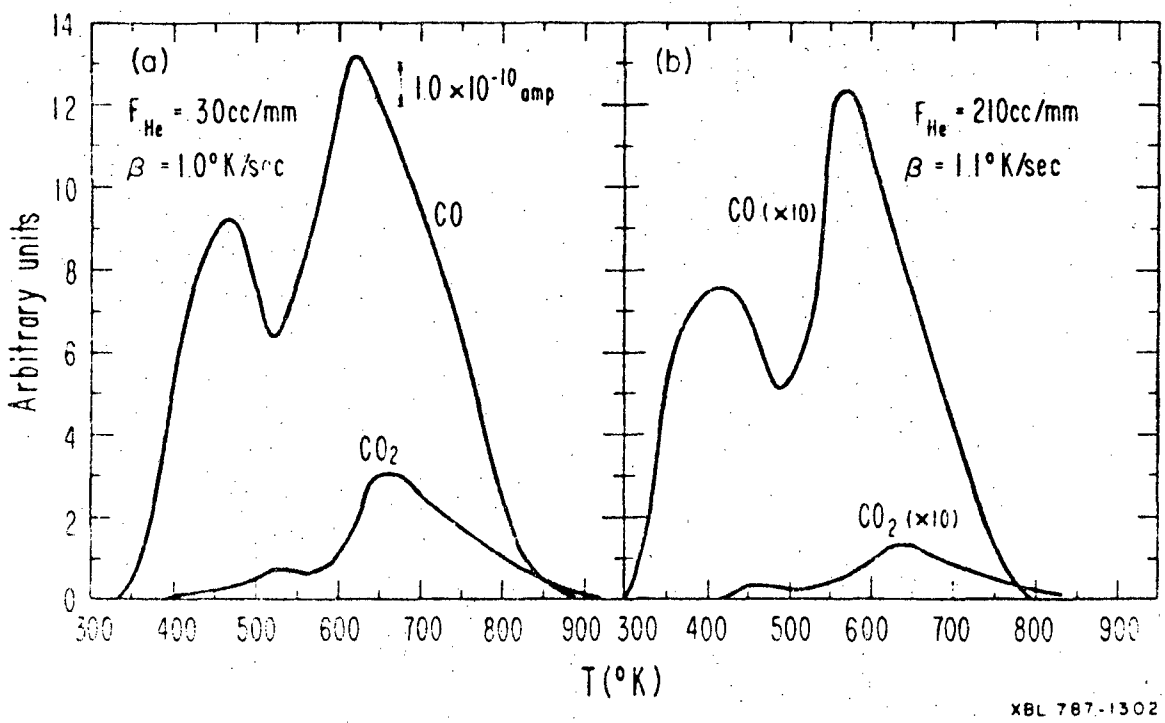
(a)
F_{He} = 30cc/mm
β = 1.0°K/sec
1.0 x 10⁻¹⁰ amp
CO
CO_2
(b)
F_{He} = 210cc/mm
β = 1.1°K/sec
CO (x10)
CO_2 (x10)
Arbitrary units
T(°K)
XBL 787-1302

Figure 1.

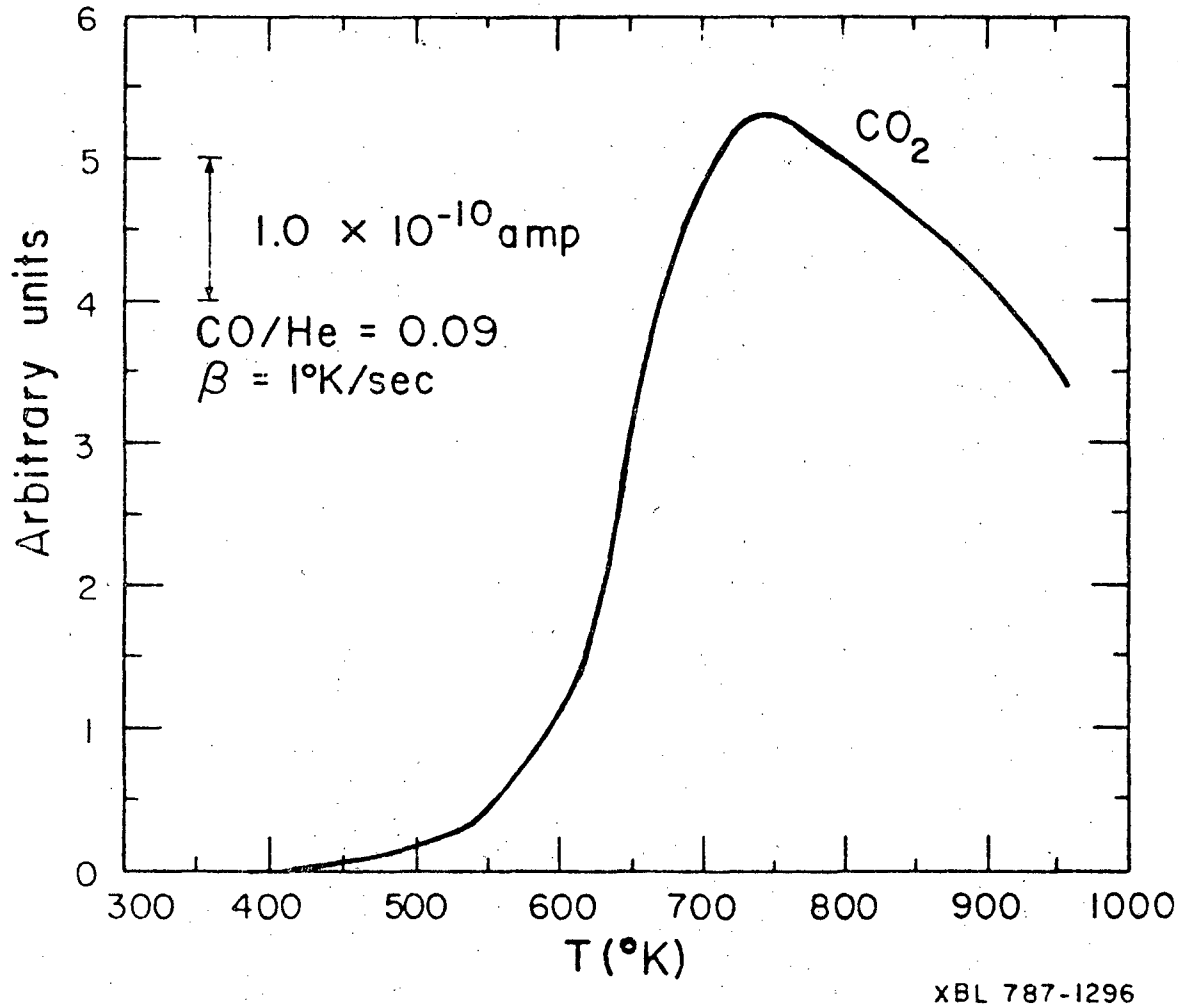
6
5
4
3
2
1
0
Arbitrary units
1.0 × 10⁻¹⁰ amp
CO/He = 0.09
β = 1°K/sec
CO2
300
400
500
600
700
800
900
1000
T (°K)
XBL 787-1296

Figure 2

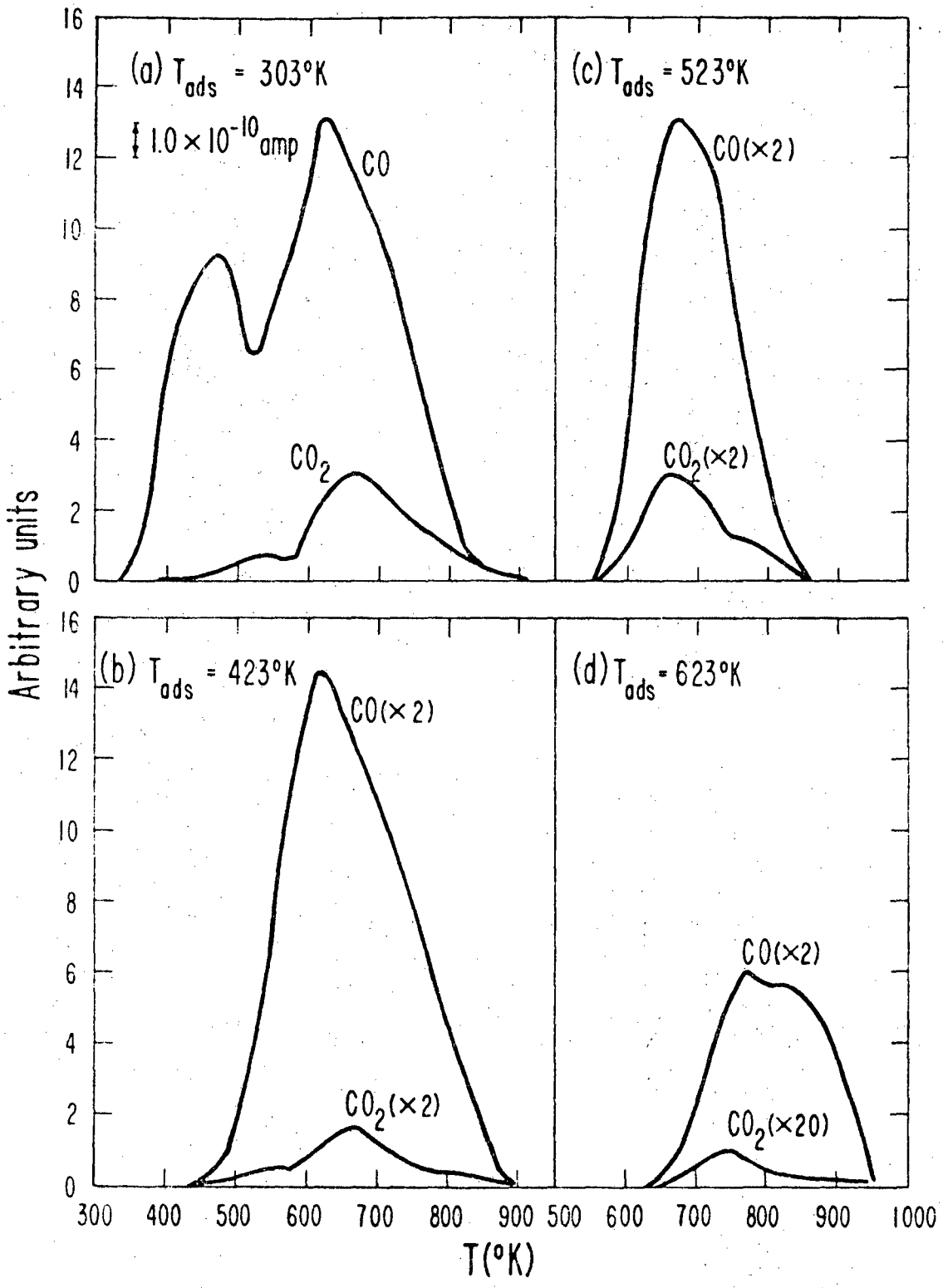
(a) T_{ads} = 303°K
1.0 × 10^{-10} amp
CO
CO_2
(c) T_{ads} = 523°K
CO(×2)
CO_2(×2)
(b) T_{ads} = 423°K
CO(×2)
CO_2(×2)
(d) T_{ads} = 623°K
CO(×2)
CO_2(×20)
Arbitrary units
T(°K)
XBL 787-1305

Figure 3

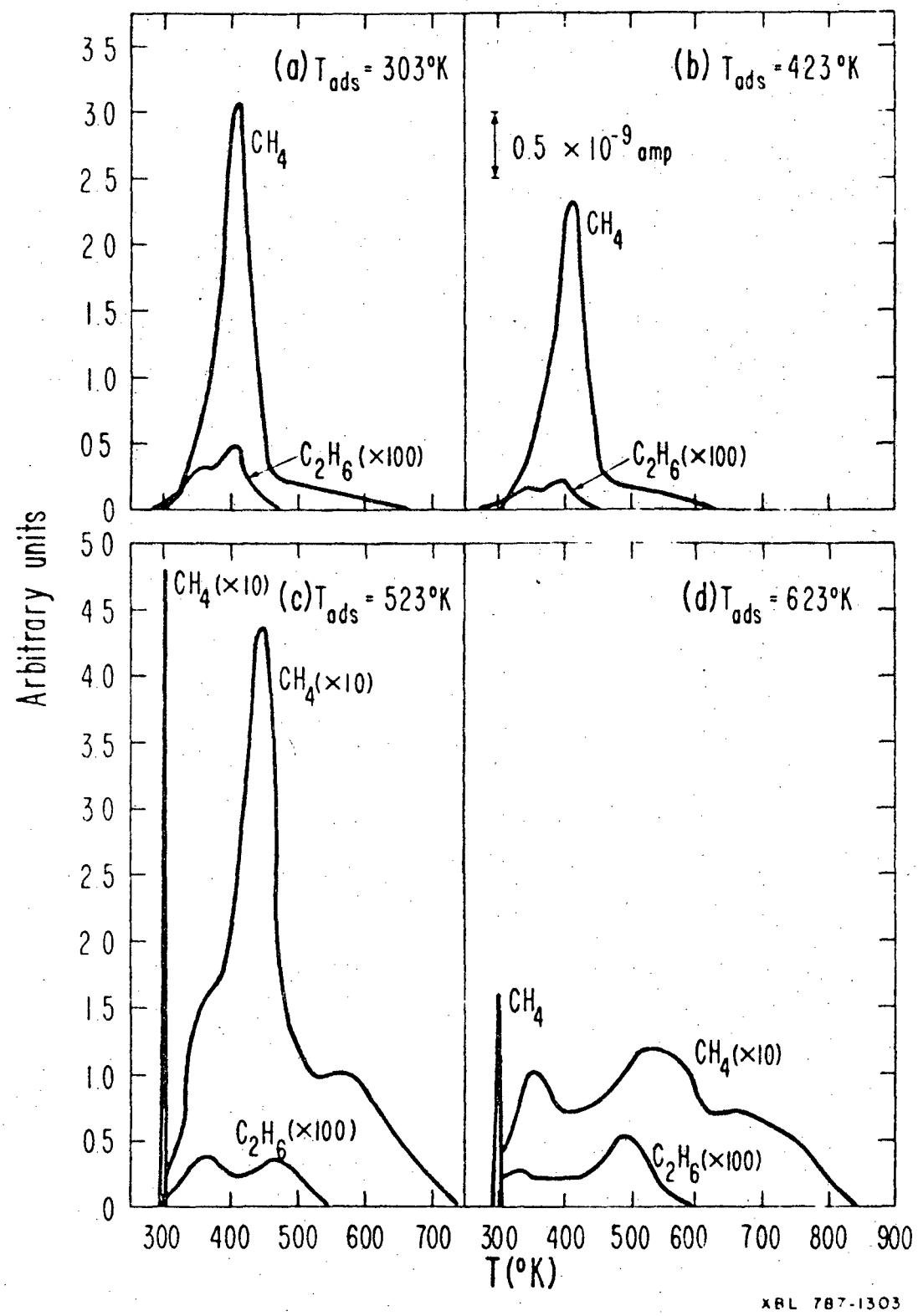
(a) T_{ads} = 303°K
CH_4
C_2H_6 (×100)
(b) T_{ads} = 423°K
0.5 × 10^{-9} amp
CH_4
C_2H_6 (×100)
CH_4 (×10)
(c) T_{ads} = 523°K
CH_4 (×10)
C_2H_6 (×100)
(d) T_{ads} = 623°K
CH_4
CH_4 (×10)
C_2H_6 (×100)
Arbitrary units
T(°K)
XBL 787-1303

Figure 4

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