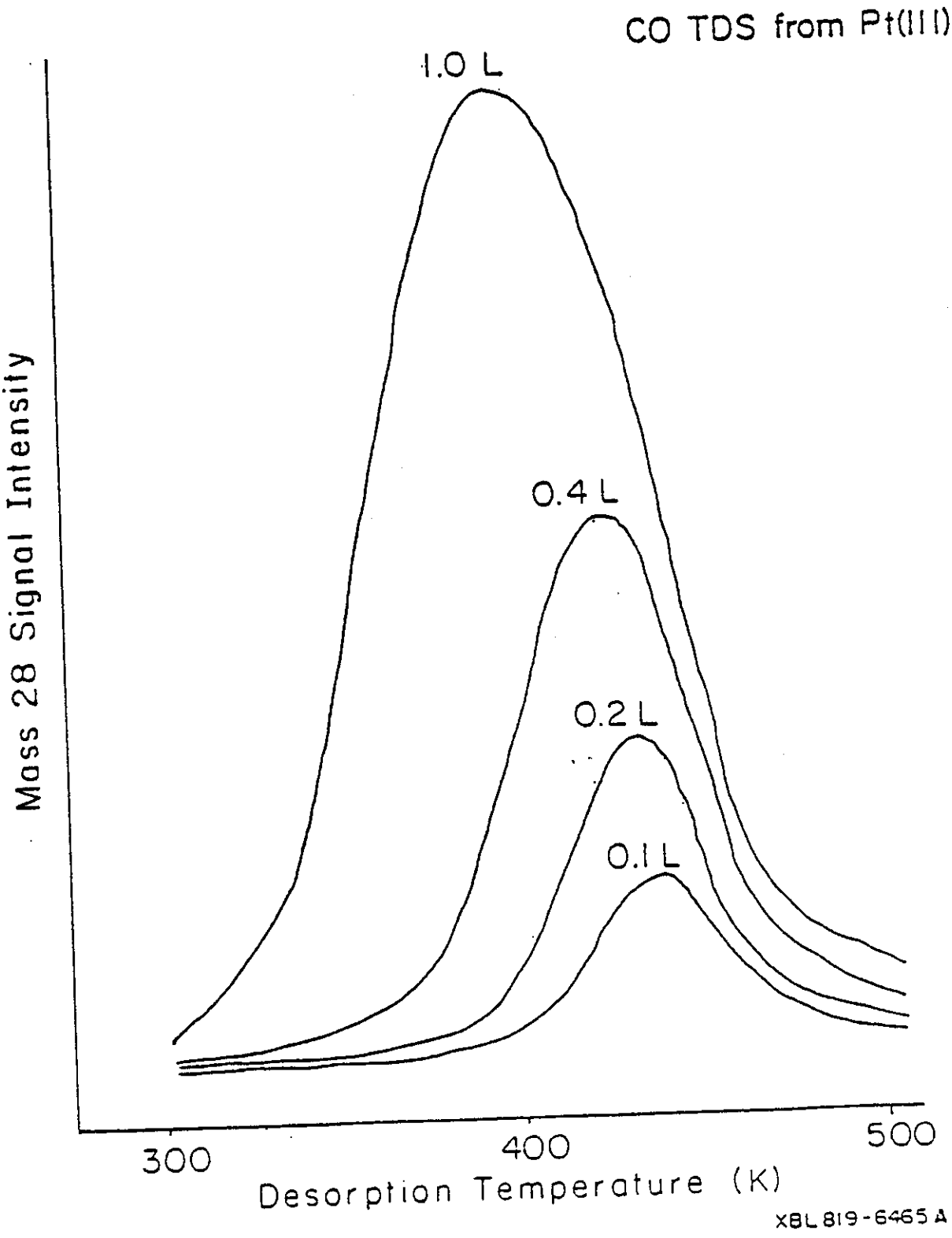


Figure 2

Thermal desorption spectra of CO from clean Pt(111) for various CO coverages (expressed in terms of Langmuirs).

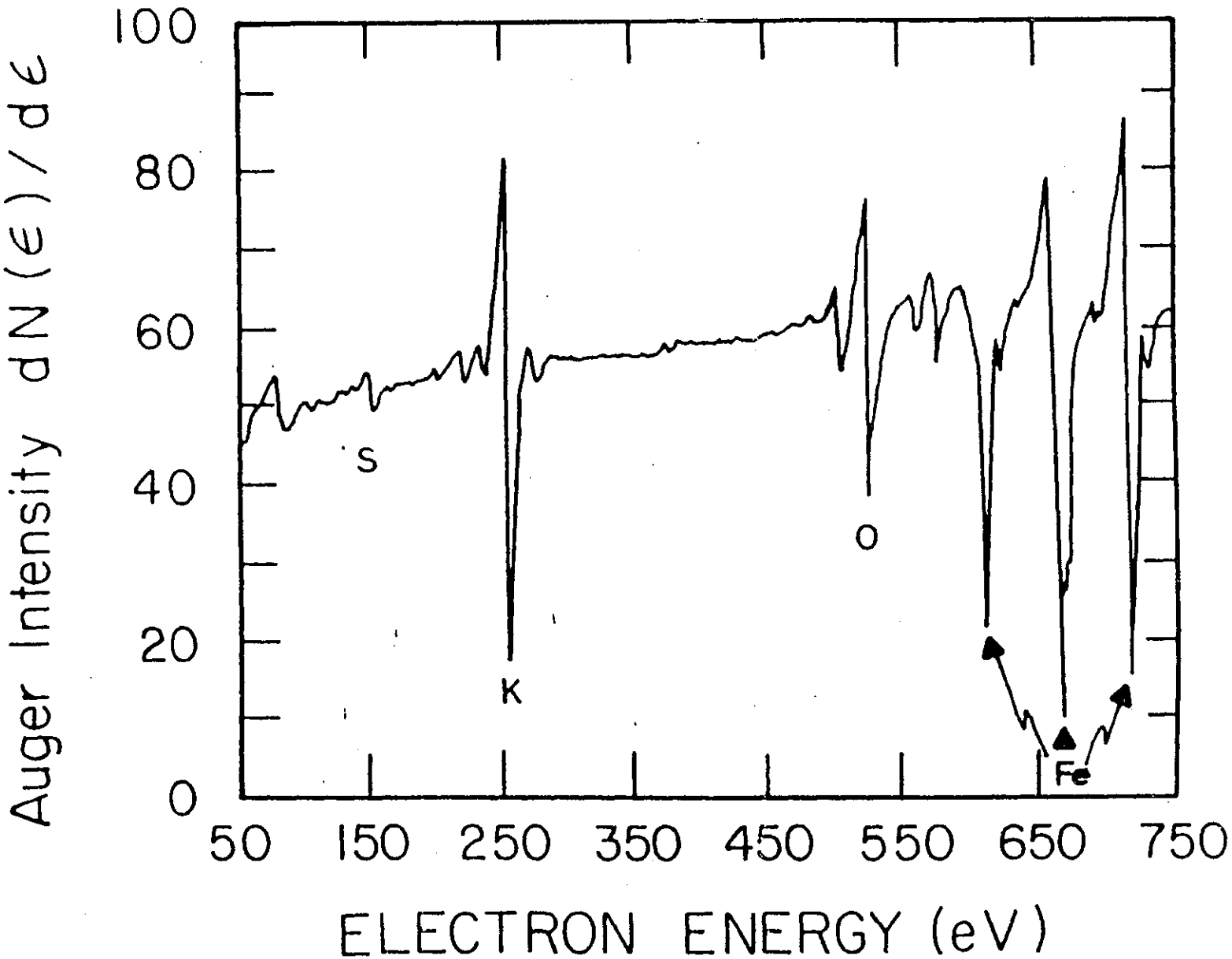


Figure 3

Auger derivative spectrum for potassium doped iron foil. Note oxygen impurity.

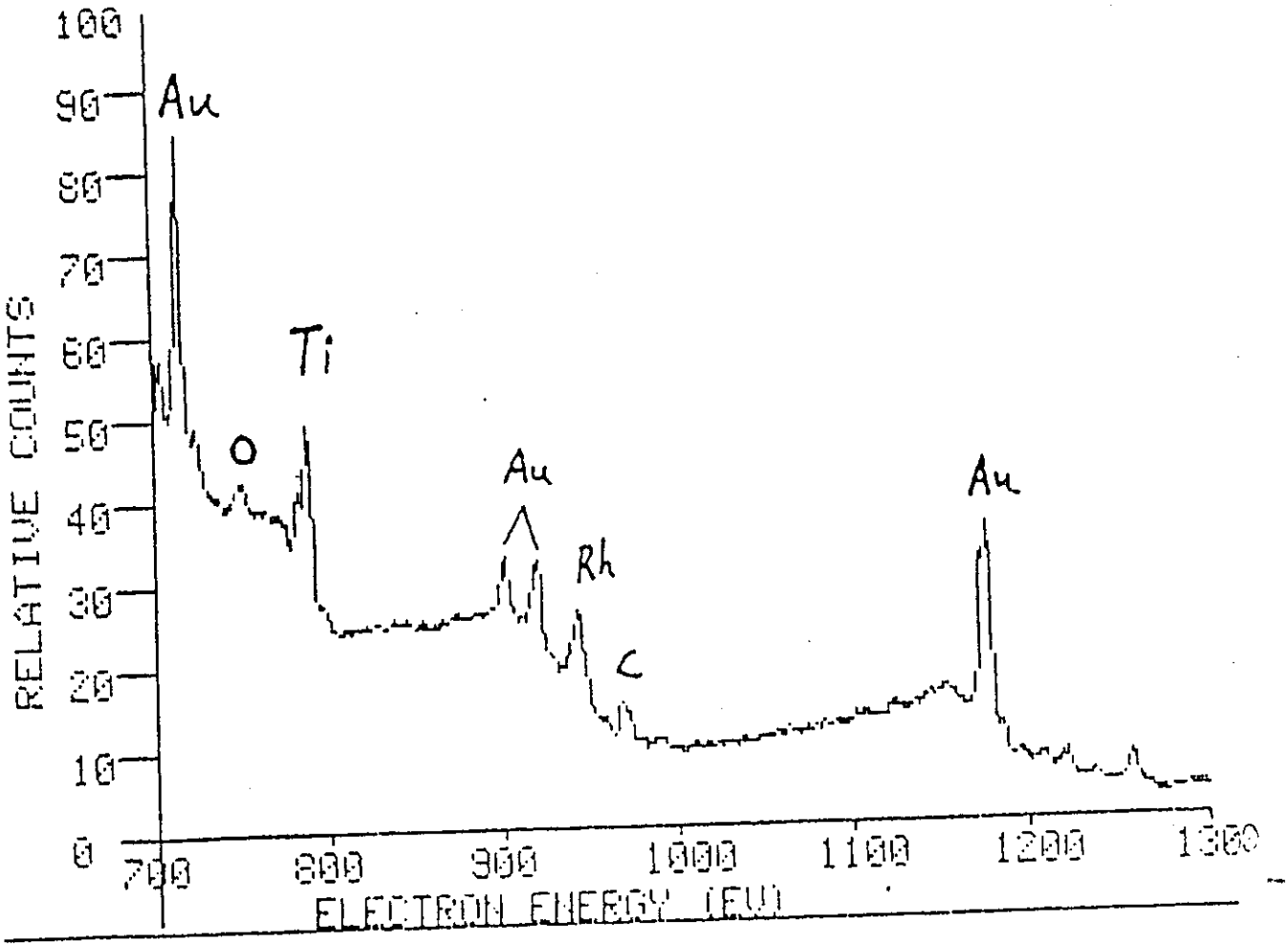


Figure 4

X-ray photoelectron spectrum of $TiRhO_3$ mounted on gold foil.

Reaction Mechanisms for the Hydrogenation of Carbon Monoxide

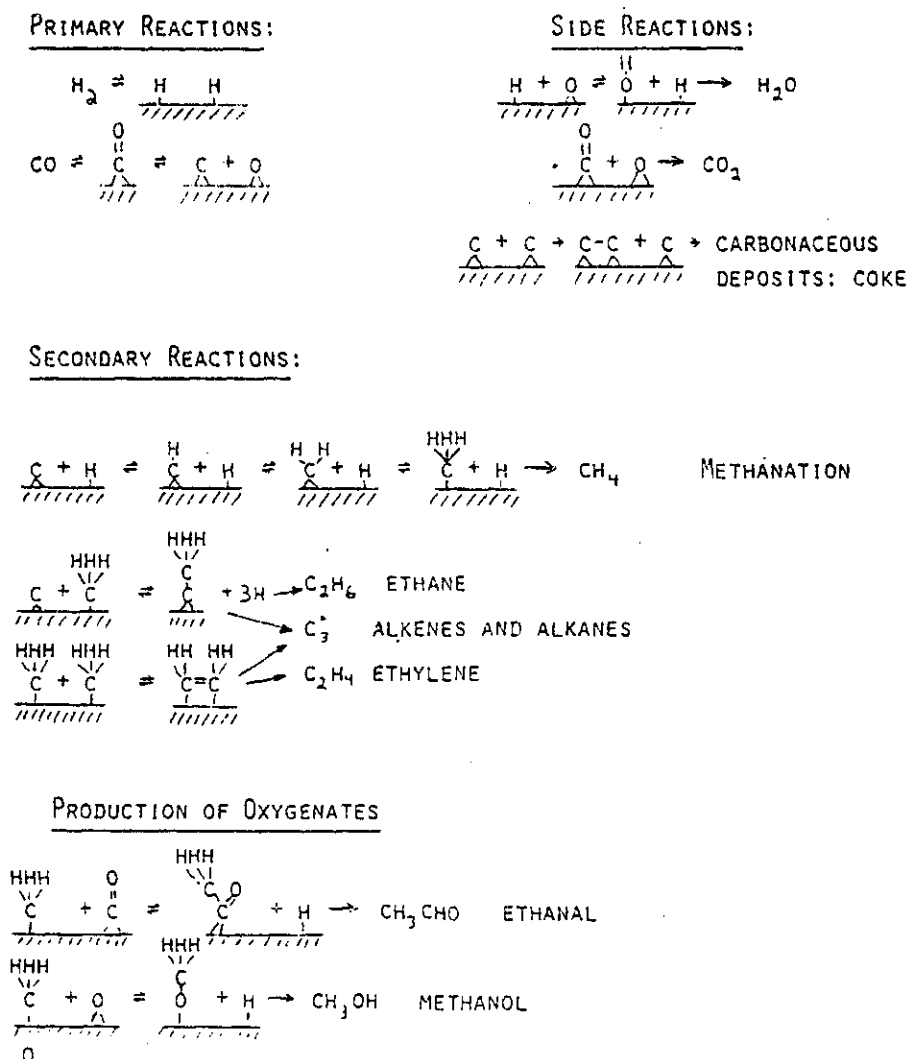


Figure 5

Possible reaction pathways for the formation of alkanes, alkenes, and oxygenated products. Also shown are the side reactions for the formation of CO_2, H_2O, and coke.

PRESSURE DEPENDENCE OF CO AND H_2 FOR METHANATION ON RHODIUM FOIL

$$R_{CH_4} = K P_{CO}^{-1} P_{H_2}^{+1}$$

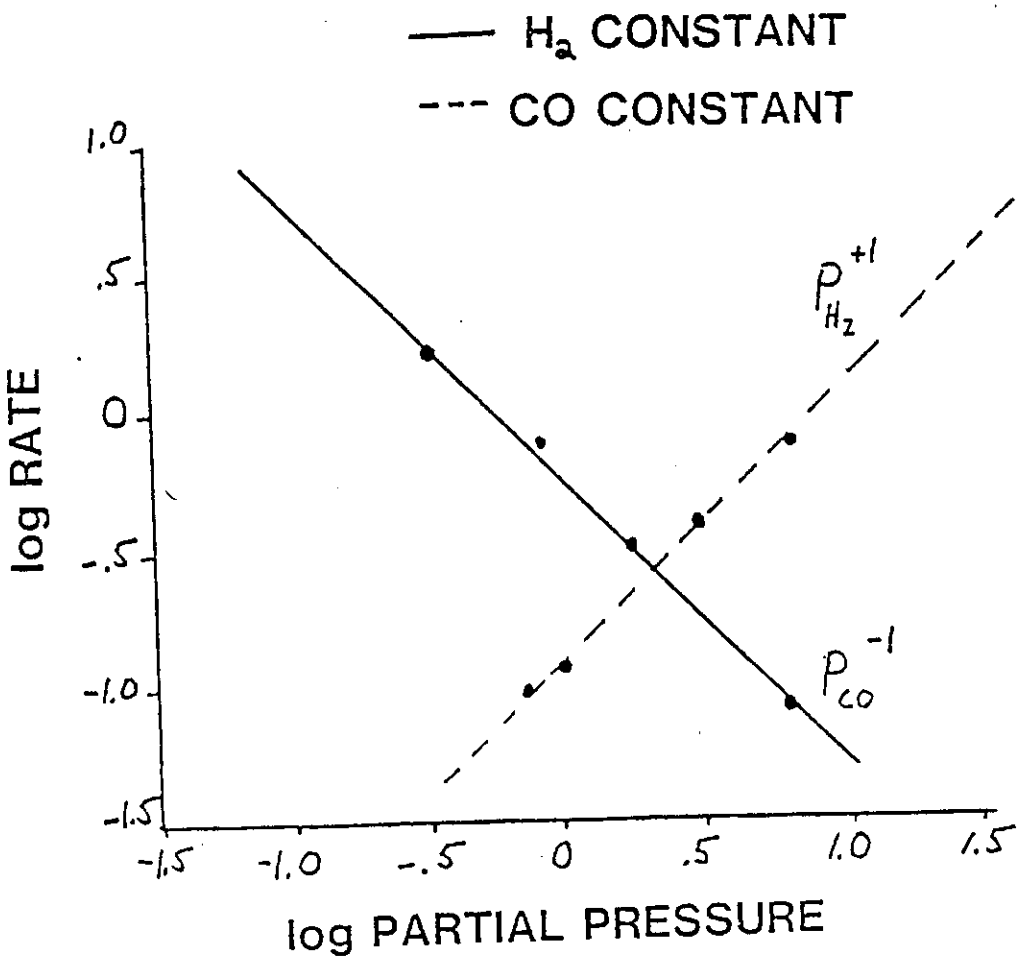


Figure 6

Experimental plot to determine the rate expression for methanation on rhodium foil.

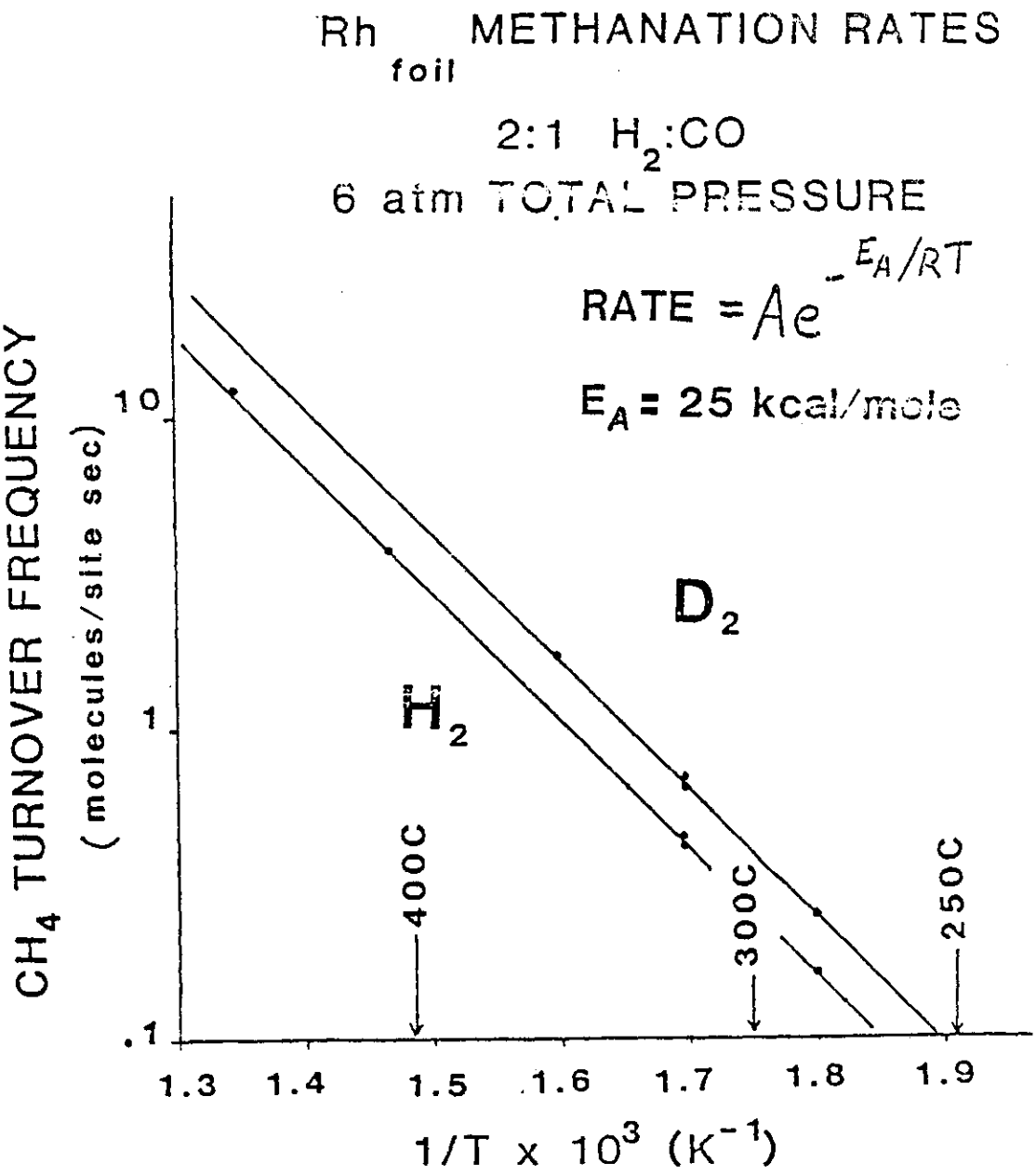


Figure 7

Rates for methanation are plotted versus temperature showing the inverse deuterium effect.

OXIDE PREPARATION / CHARACTERIZATION

1) MIX WATER SOLUBLE SALTS

2) PRECIPITATE WITH AMMONIUM CARBONATE

3) FIRE CARBONATE PRECIPITATE AT 500°C
(IN AIR FOR 12 HOURS)

4) GRIND OXIDE TO PASS THROUGH 400 MESH SCREEN

5) CHARACTERIZE OXIDE WITH A) SEM
B) X-RAY DIFFRACTION

6) BET SURFACE AREA DETERMINATION

7) MOUNT ON GOLD FOIL

8) AUGER ELECTRON SPECTROSCOPY

9) X-RAY PHOTOELECTRON SPECTROSCOPY

Figure 8
Procedure for preparing and characterizing oxide samples.

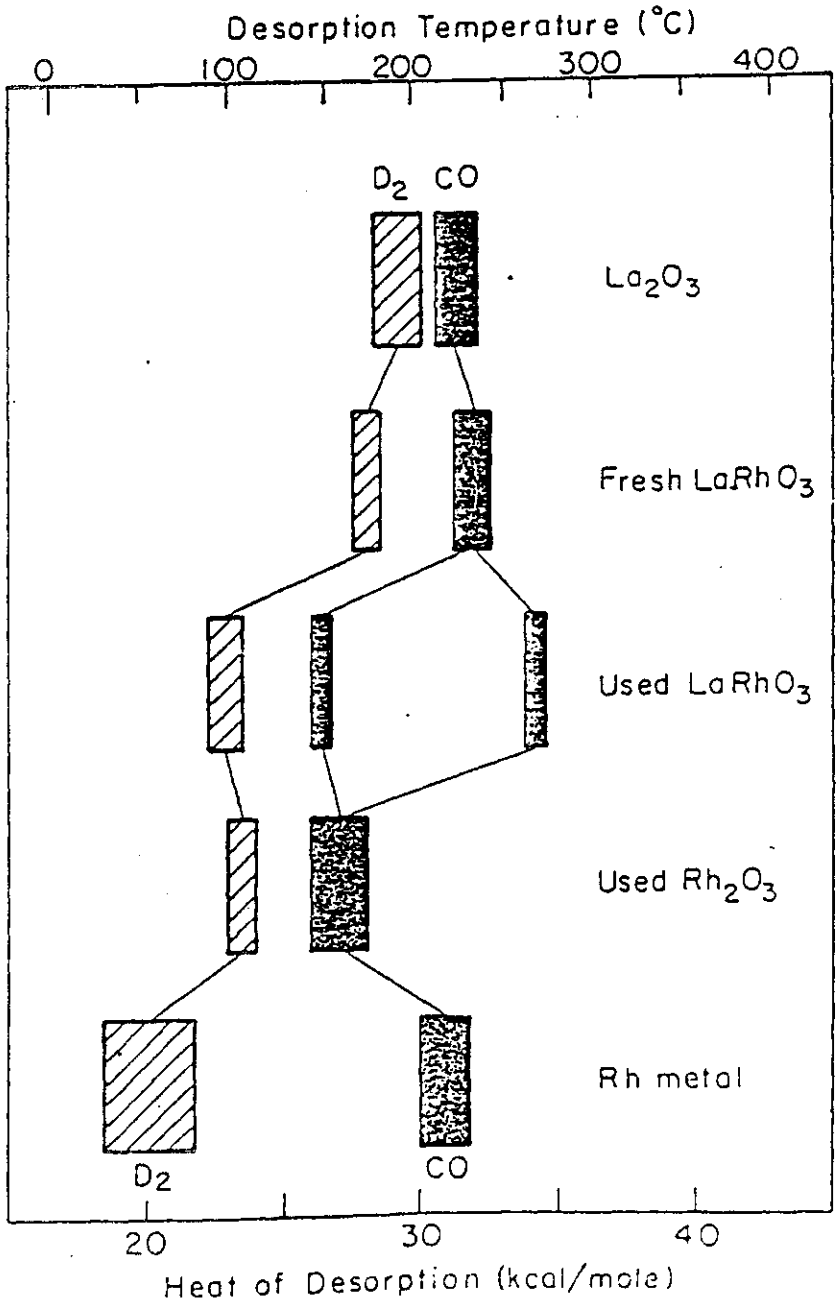


Figure 9

Thermal desorption results from CO and D_2 showing the two binding states of CO on the used $LaRhO_3$ catalyst . Also an apparent correlation between the D_2 heat of desorption and the oxidation state of rhodium on the surface can be seen.

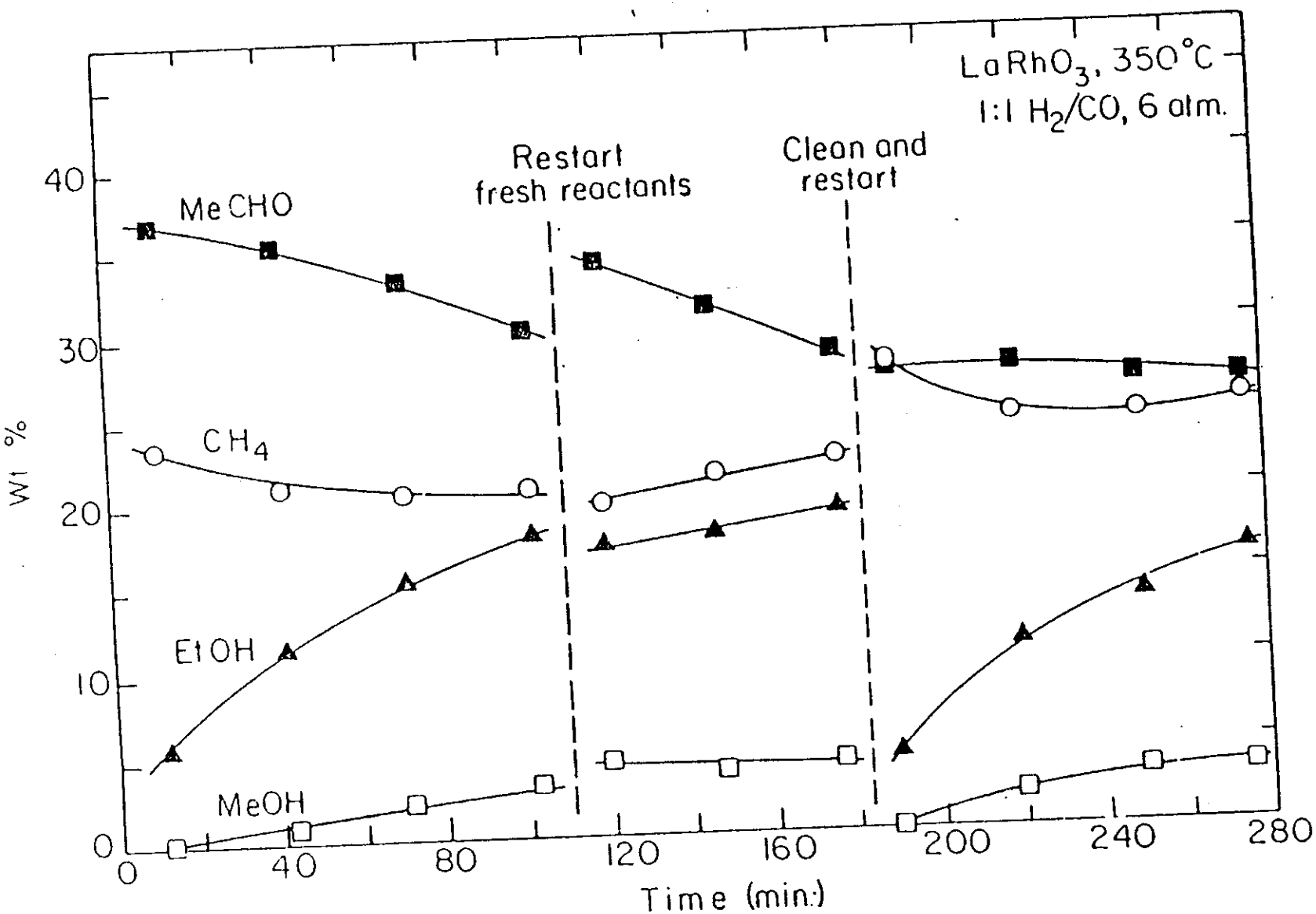


Figure 10

The change in product distribution with time is shown for methane, methanol, ethanal, and ethanol, showing the effect of replenishing the reactants, and cleaning the sample and using fresh reactants.

Compound	Rh_{foil}	Na_2RhO_3	$TiRhO_3$	$CuRh_2O_4$	$FeRhO_3$	$LaRhO_3$
CH_4 Turnover Frequency	0.37	0.08	0.07	~0.001	0.03	0.06

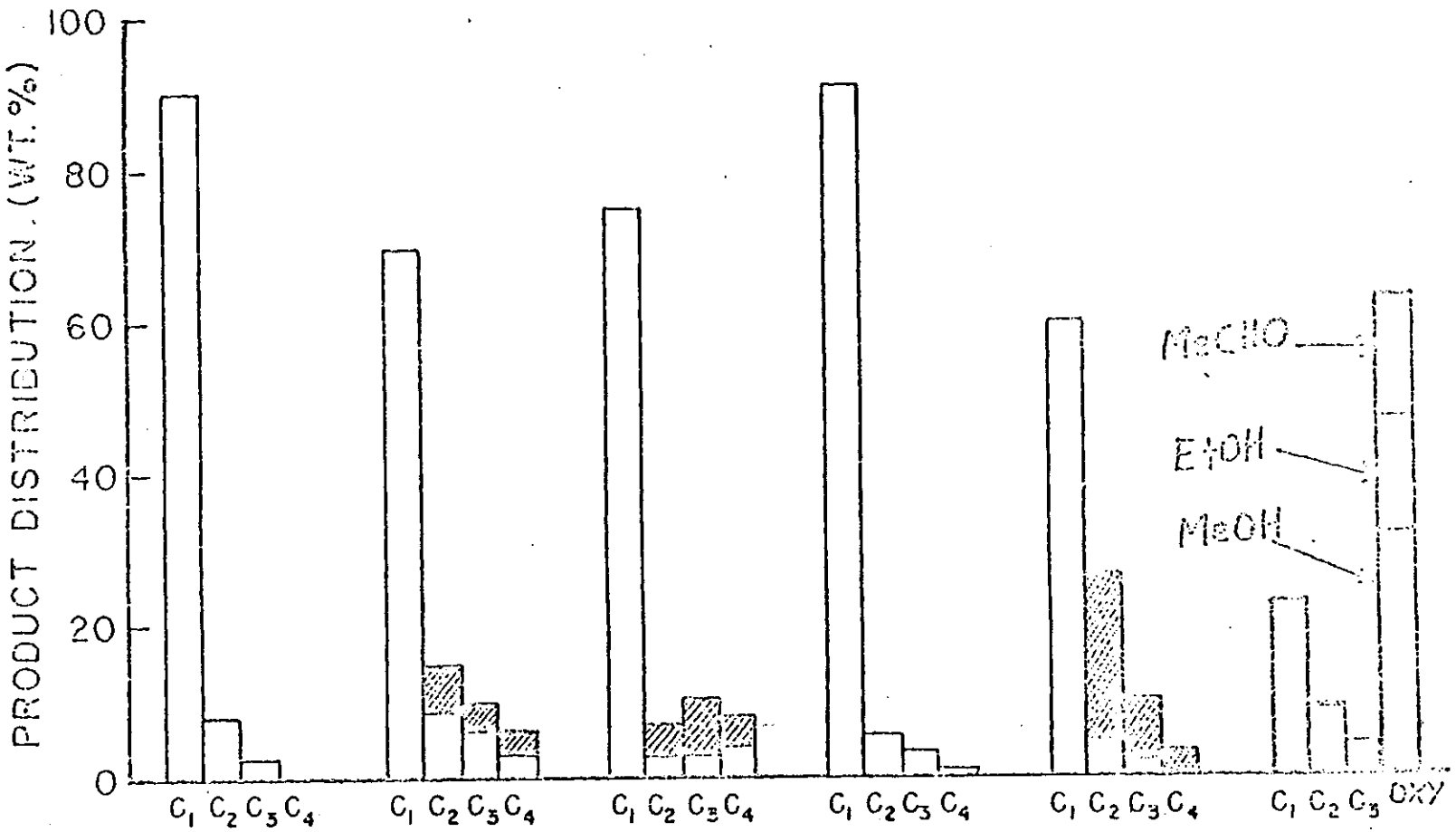


Figure 11

Product distributions for several rhodium compounds. CH_4 turnover frequency = molecules of CH_4 produced per site per second. Shaded areas represent alkene formation while open areas represent alkane formation.

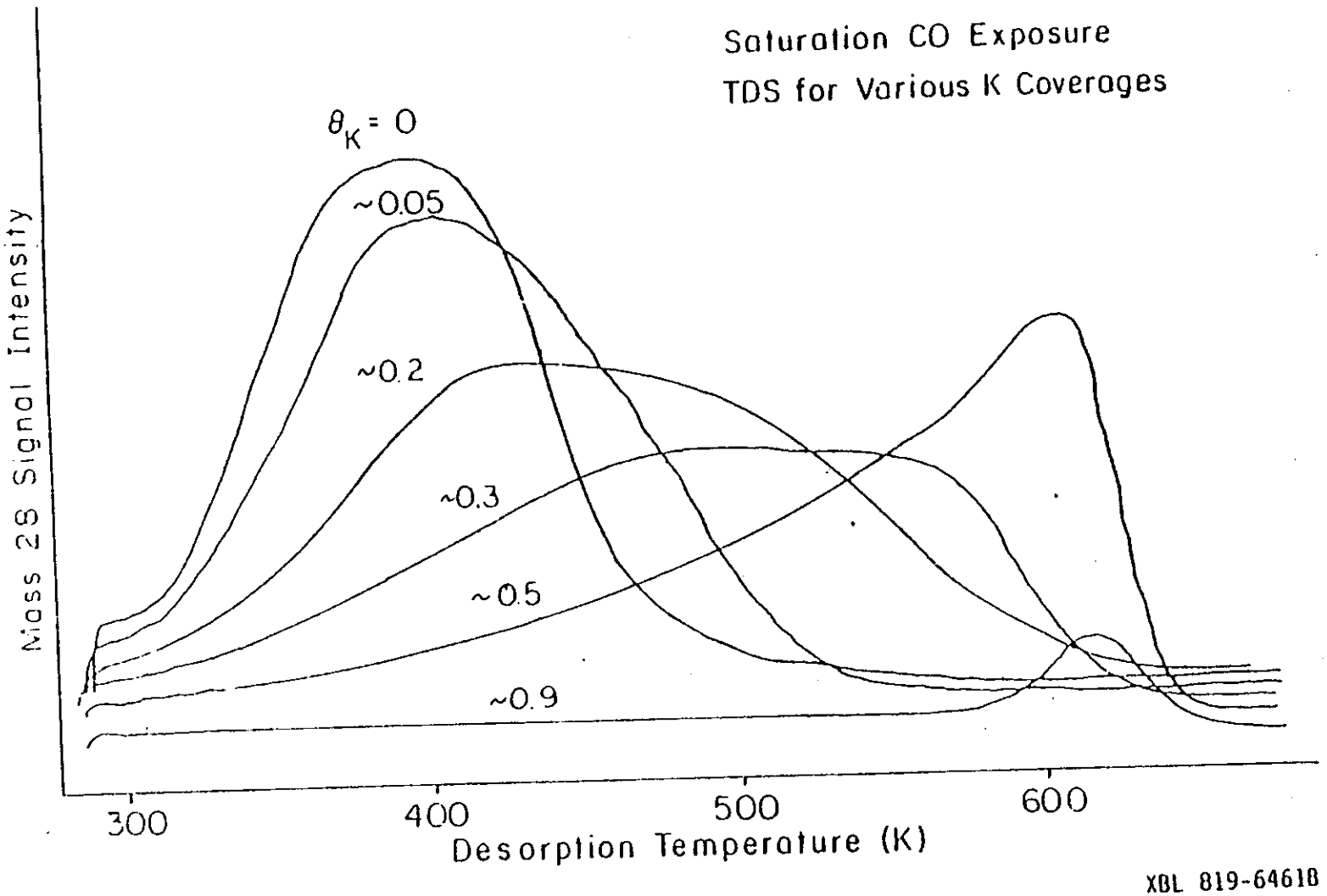


Figure 12

CO thermal desorption spectra with various potassium coverages, after saturation CO exposures (~10 L).

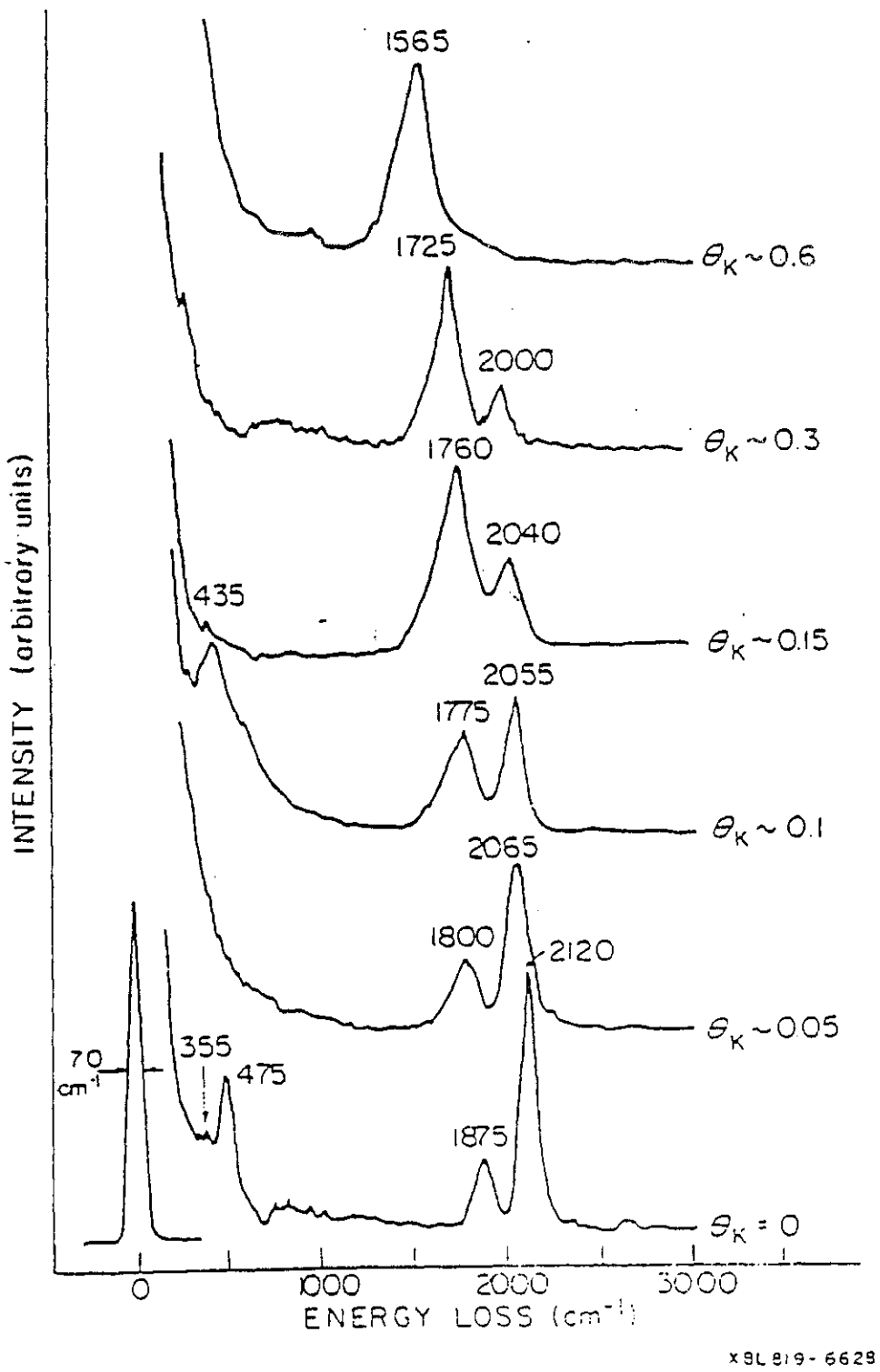


Figure 13

HREELS spectra for saturation CO exposures with various potassium coverages.

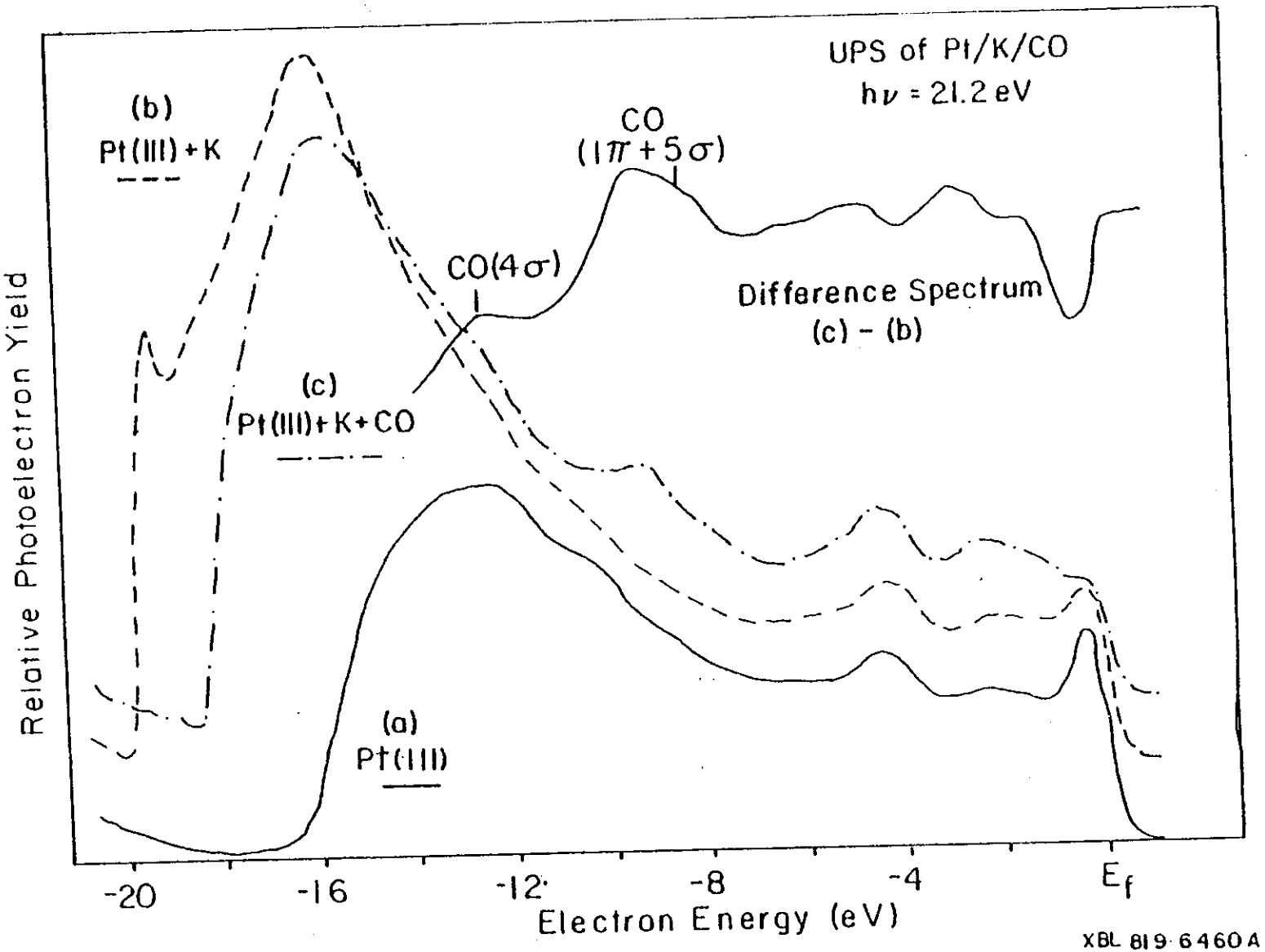
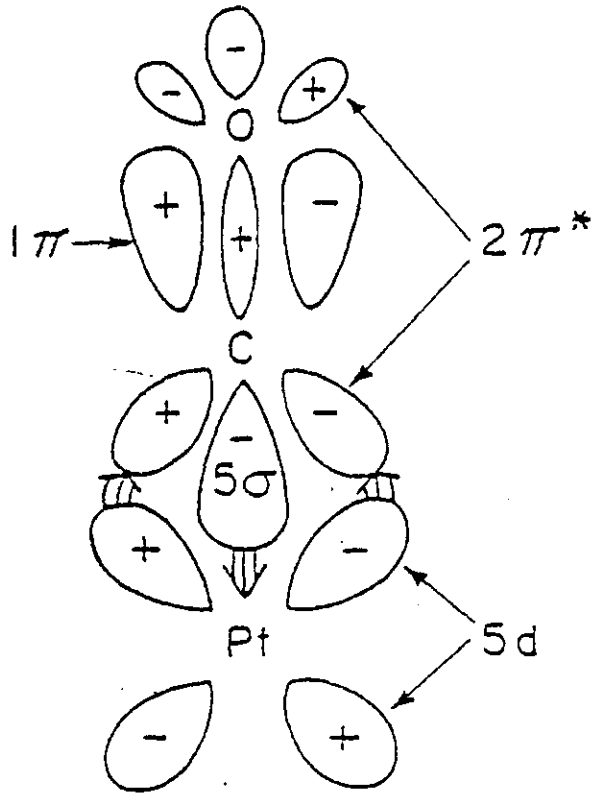
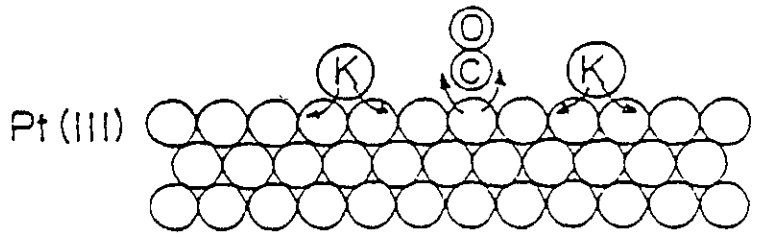


Figure 14

UPS spectra for (a) the potassium free Pt(111) surface, (b) the Pt(111) surface with θ_K=0.33, and (c) the θ_K=0.33 surface after exposure to 10L of CO. Note the change in work function.





XBL823-8332

Figure 15

(a) A model of the electron orbitals believed to interact most strongly in the bonding of CO to platinum. (b) A schematic diagram of electron transfer in the Pt(111)/K/CO system.

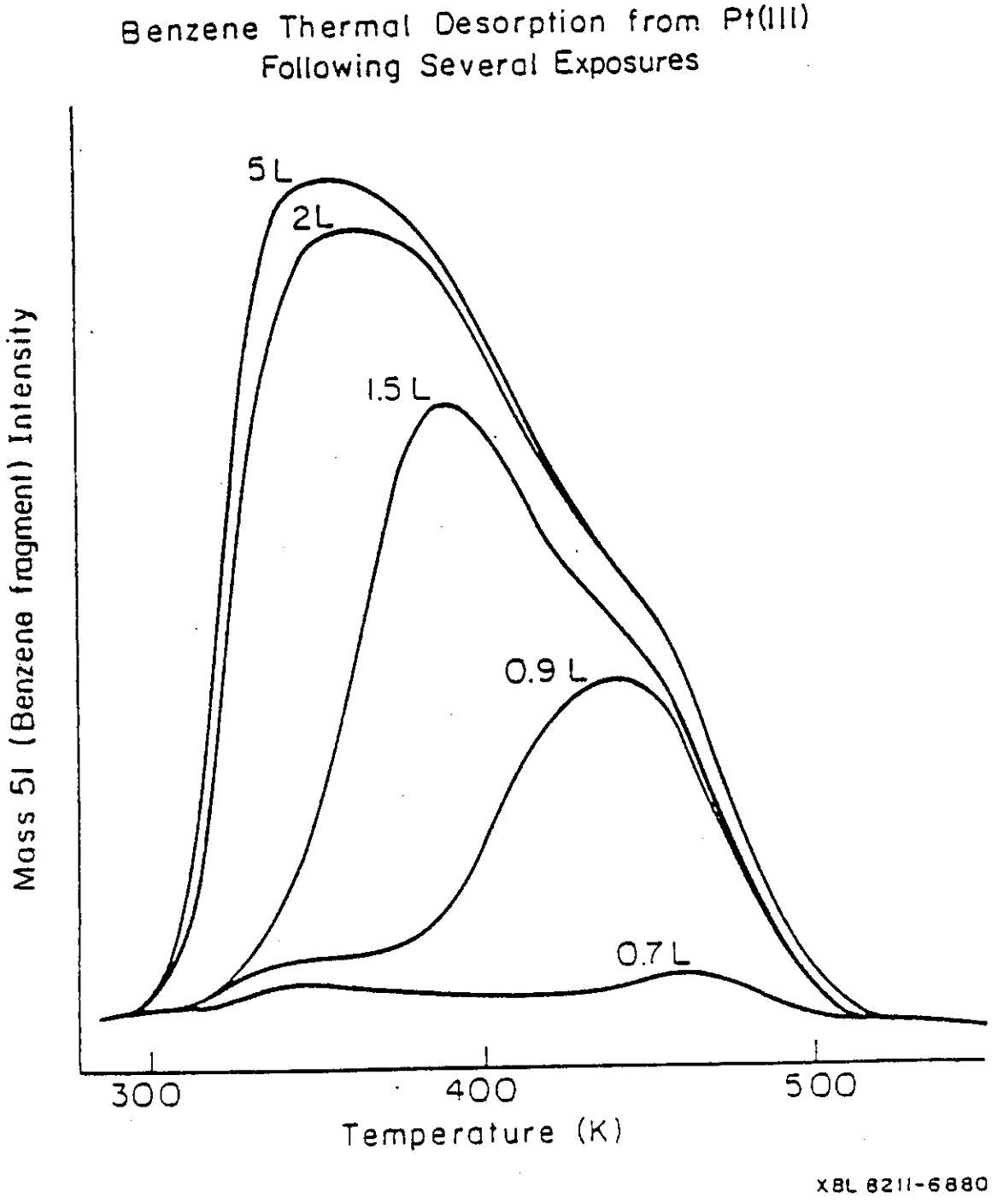


Figure 16

Benzene thermal desorption spectra following several exposures.

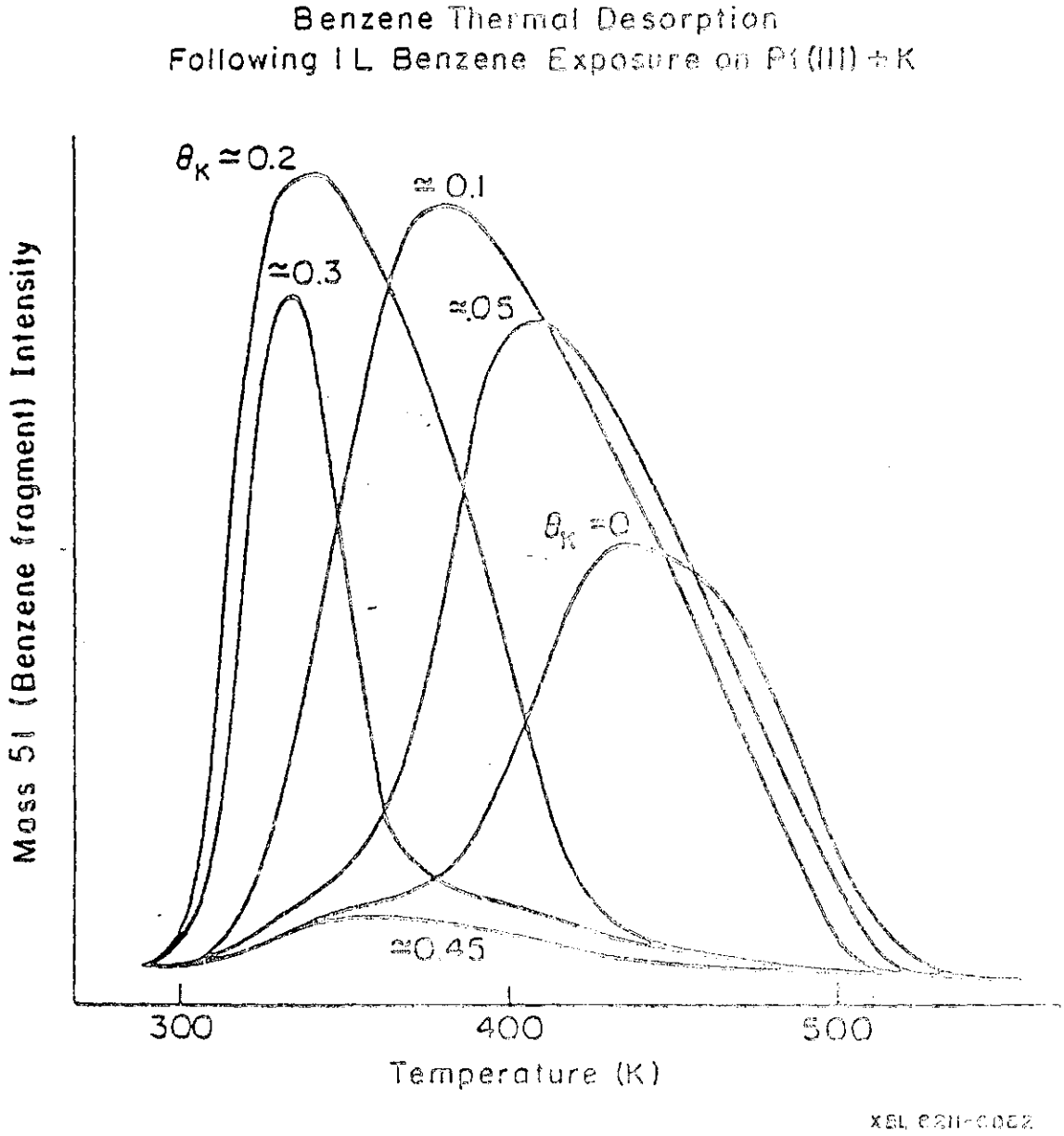


Figure 17

Benzene TDS from Pt(111) following 5 L exposures. (Heating rate = 30 K/s). Note that a potassium monolayer (saturation) is defined such that θ_K=1 and is about 1/3 the atomic density of the platinum surface layer.

Valence Orbitals of Benzene-Cr: Energy levels are approximate

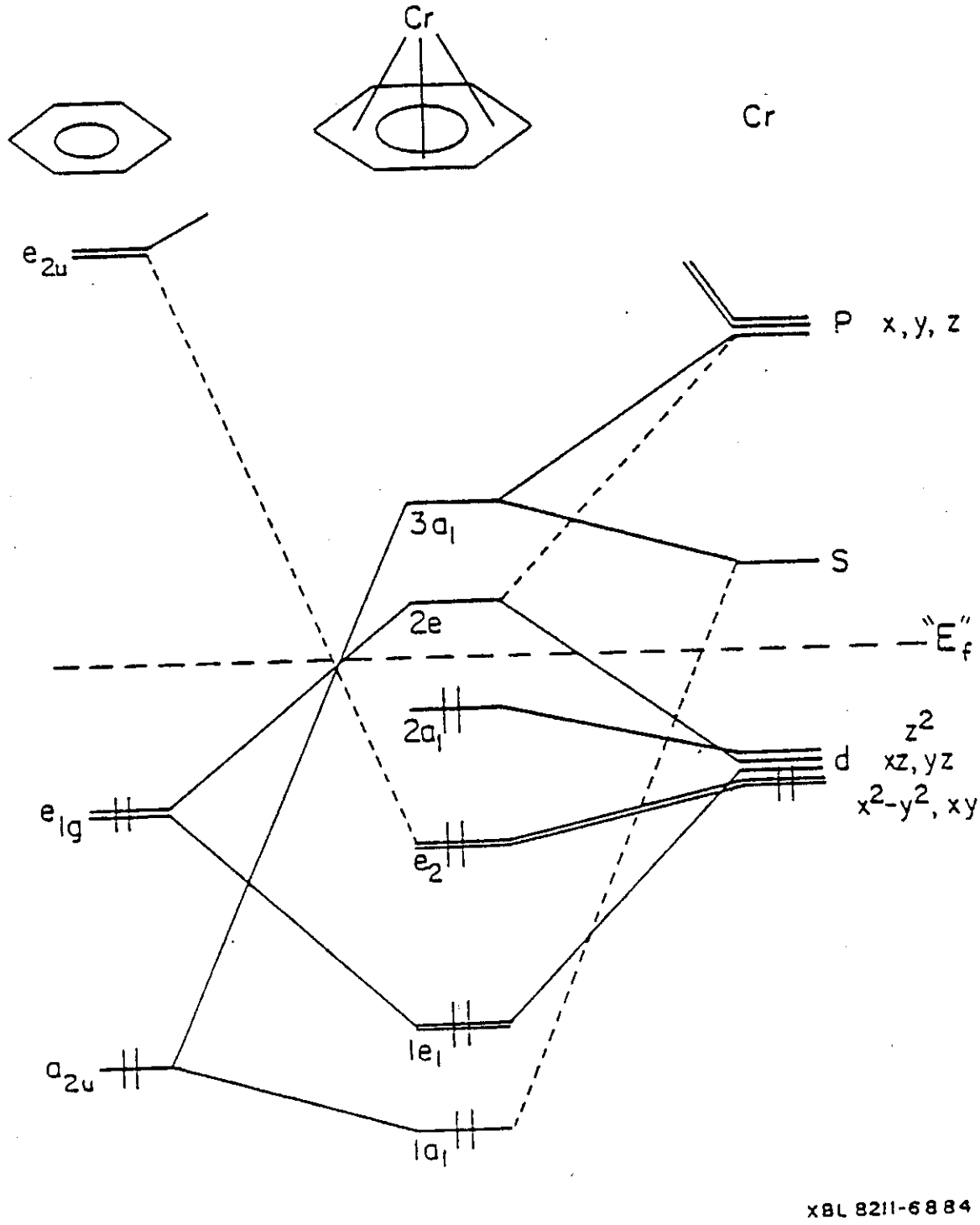


Figure 18

Molecular orbital correlation diagram for dibenzene-chromium

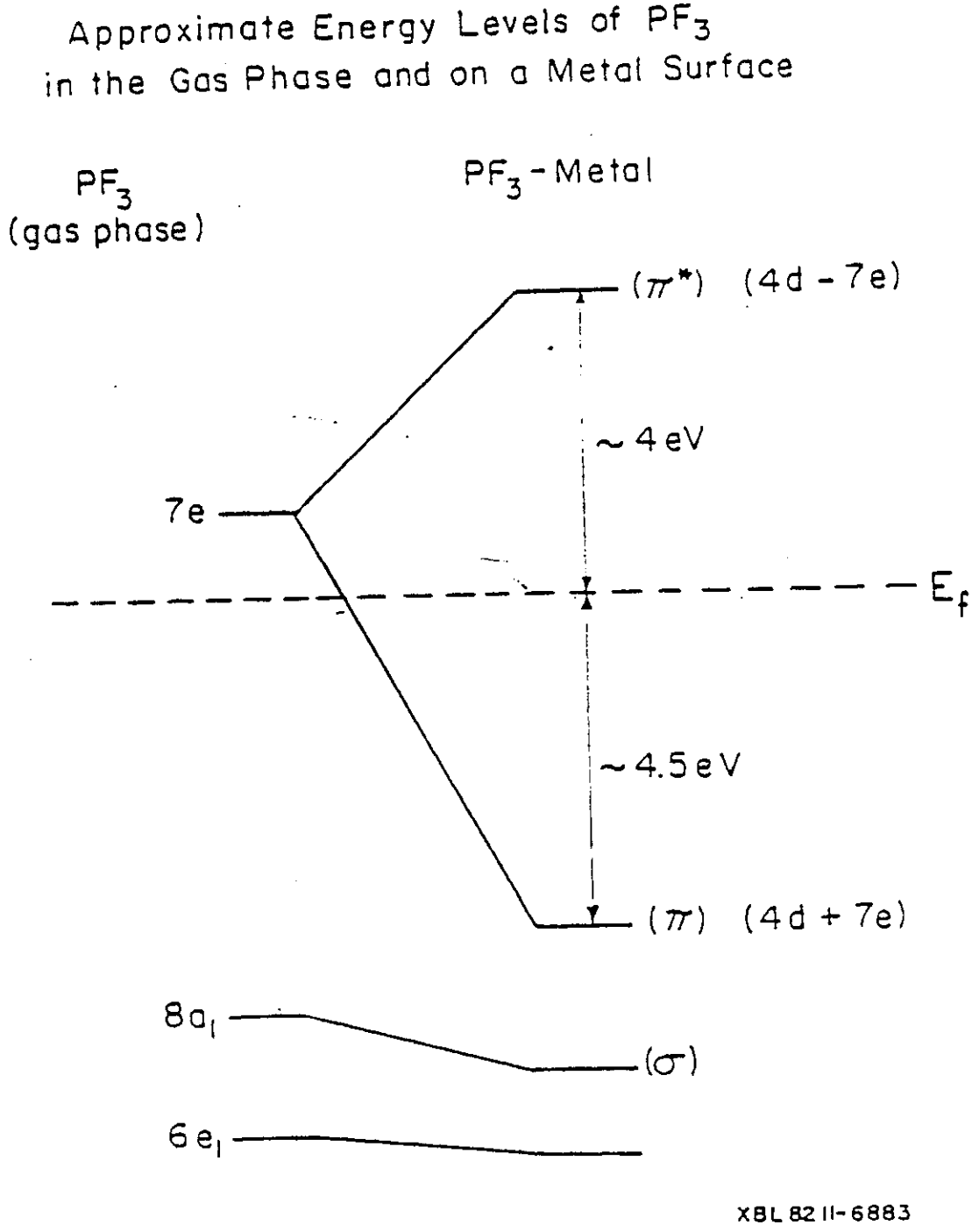


Figure 19

Approximate positions of orbital energies for PF_3. Both gas phase and chemisorption positions are given.

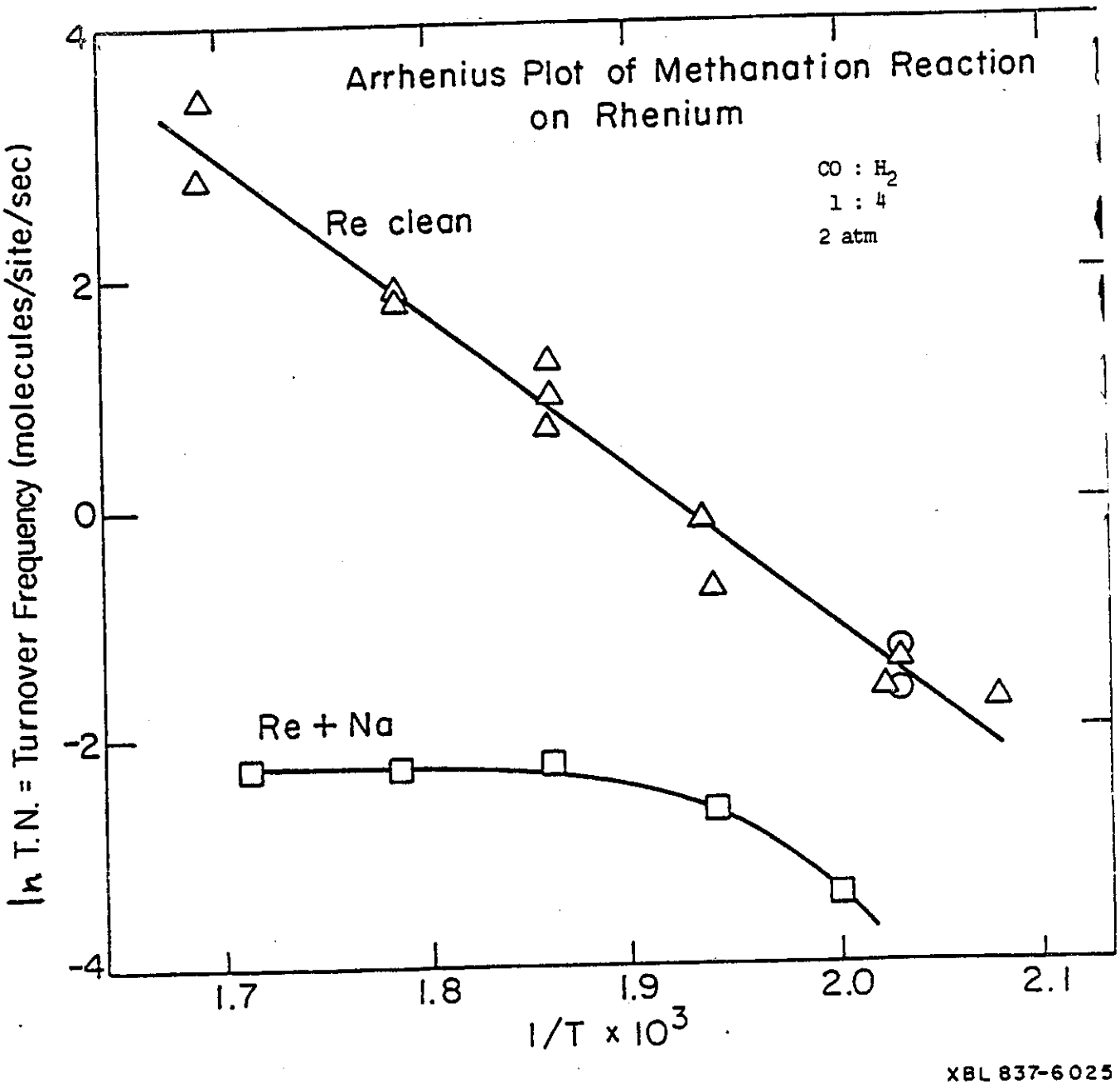
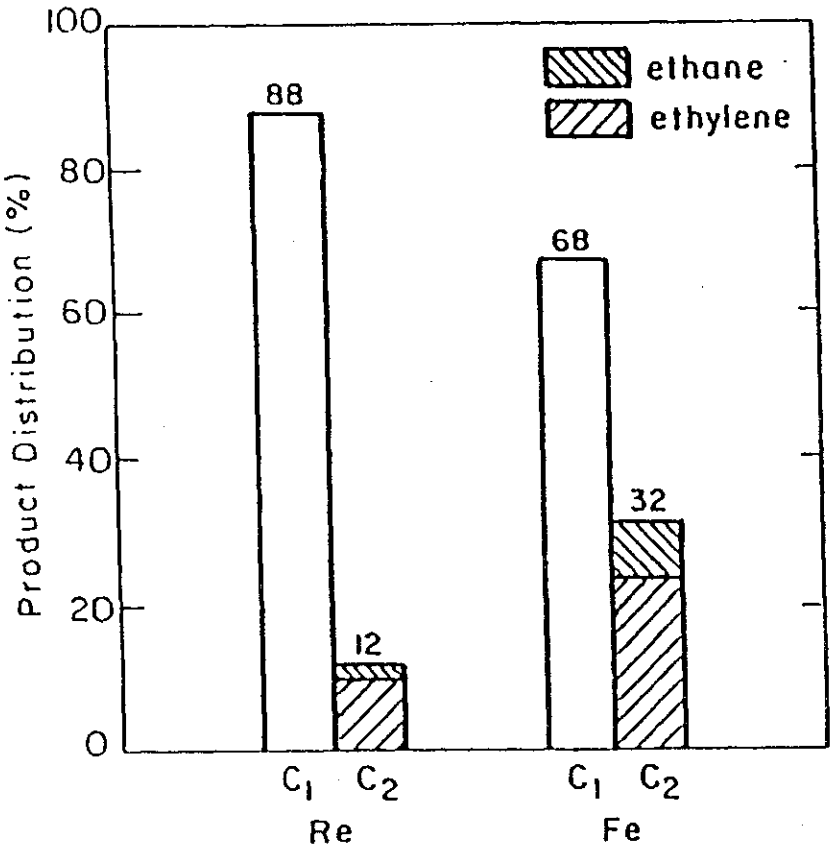

Arrhenius Plot of Methanation Reaction
on Rhenium
CO : H2
1 : 4
2 atm
Re clean
Re + Na
ln T.N. = Turnover Frequency (molecules/site/sec)
1/T x 10^3
4
2
0
-2
-4
1.7
1.8
1.9
2.0
2.1
XBL 837-6025

Figure 20



CO Hydrogenation
540 K $CO/H_2 = 1/4$
32 psi

	Re	Fe
Turnover Frequency (molecules/site/sec)	2	5
$E_a(CH_4)$ kcal/mole	28	24
$E_a(C_2H_4)$ kcal/mole	21	17

XBL 837-6026

Figure 21a

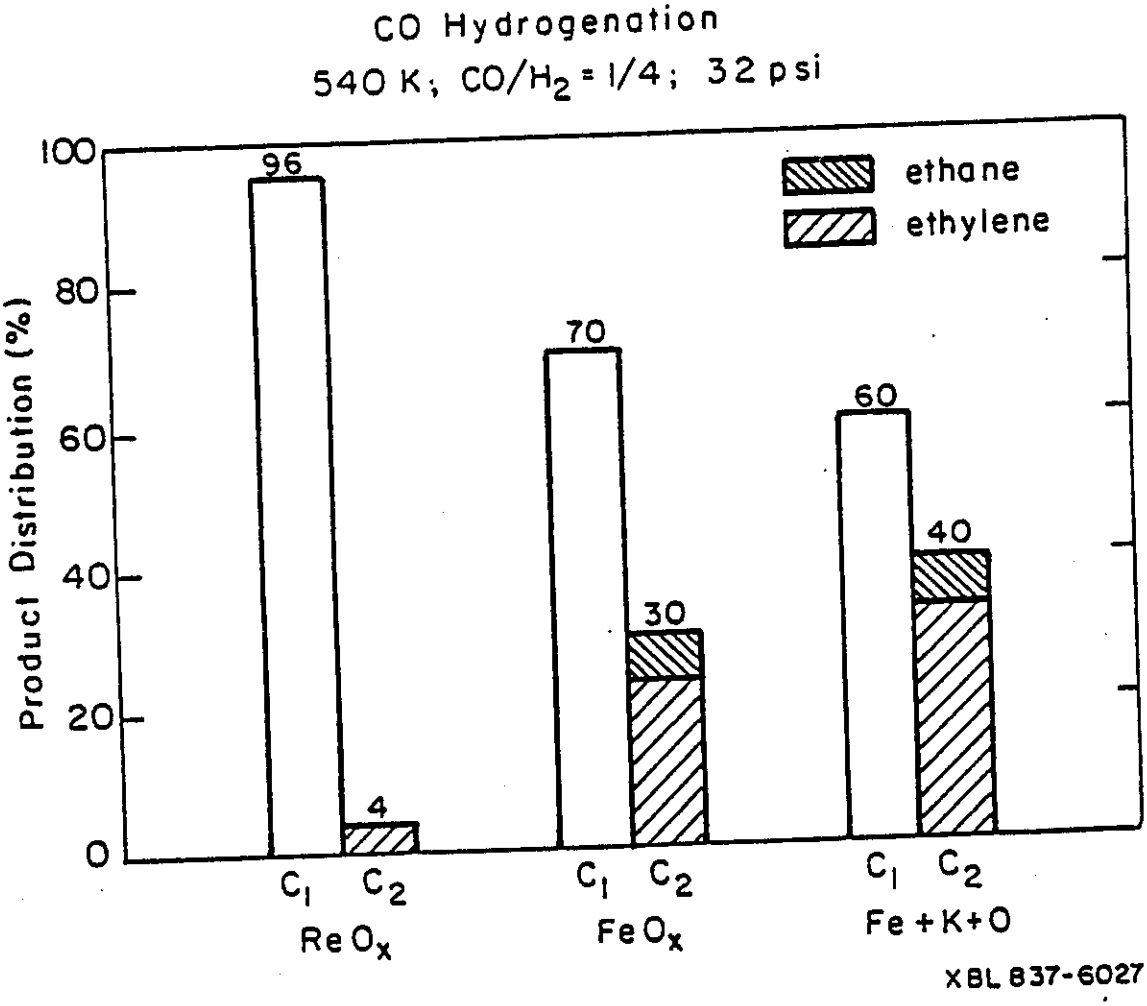

CO Hydrogenation
540 K; CO/H2 = 1/4; 32 psi
Product Distribution (%)
100
80
60
40
20
0
96
4
70
30
60
40
ethane
ethylene
C1
C2
ReOx
FeOx
Fe+K+O
XBL 837-6027

Figure 21b

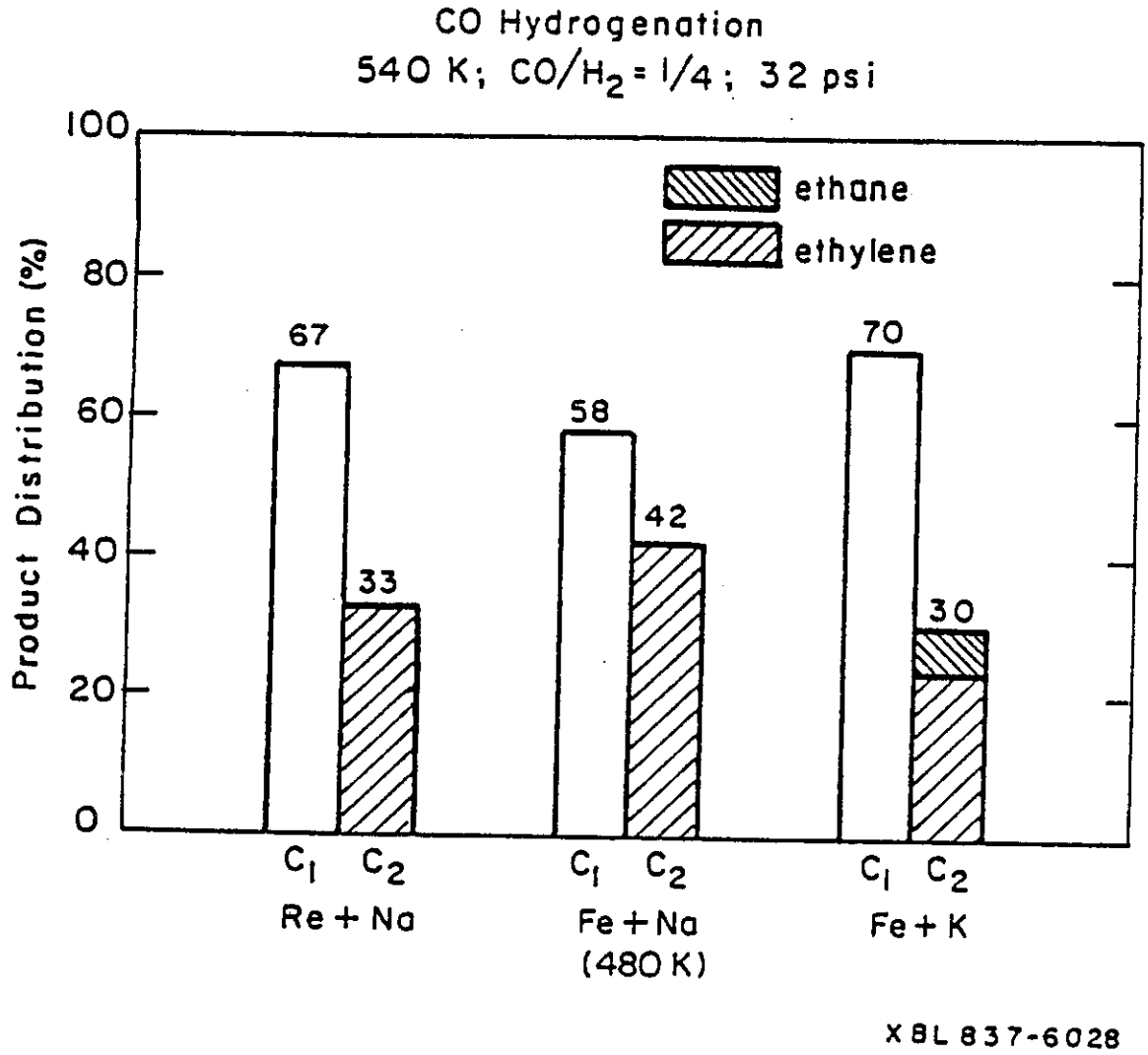

CO Hydrogenation
540 K; CO/H2 = 1/4; 32 psi
Product Distribution (%)
100
80
60
40
20
0
ethane
ethylene
67
33
58
42
70
30
C1 C2
Re + Na
C1 C2
Fe + Na
(480 K)
C1 C2
Fe + K
XBL 837-6028

Figure 21c

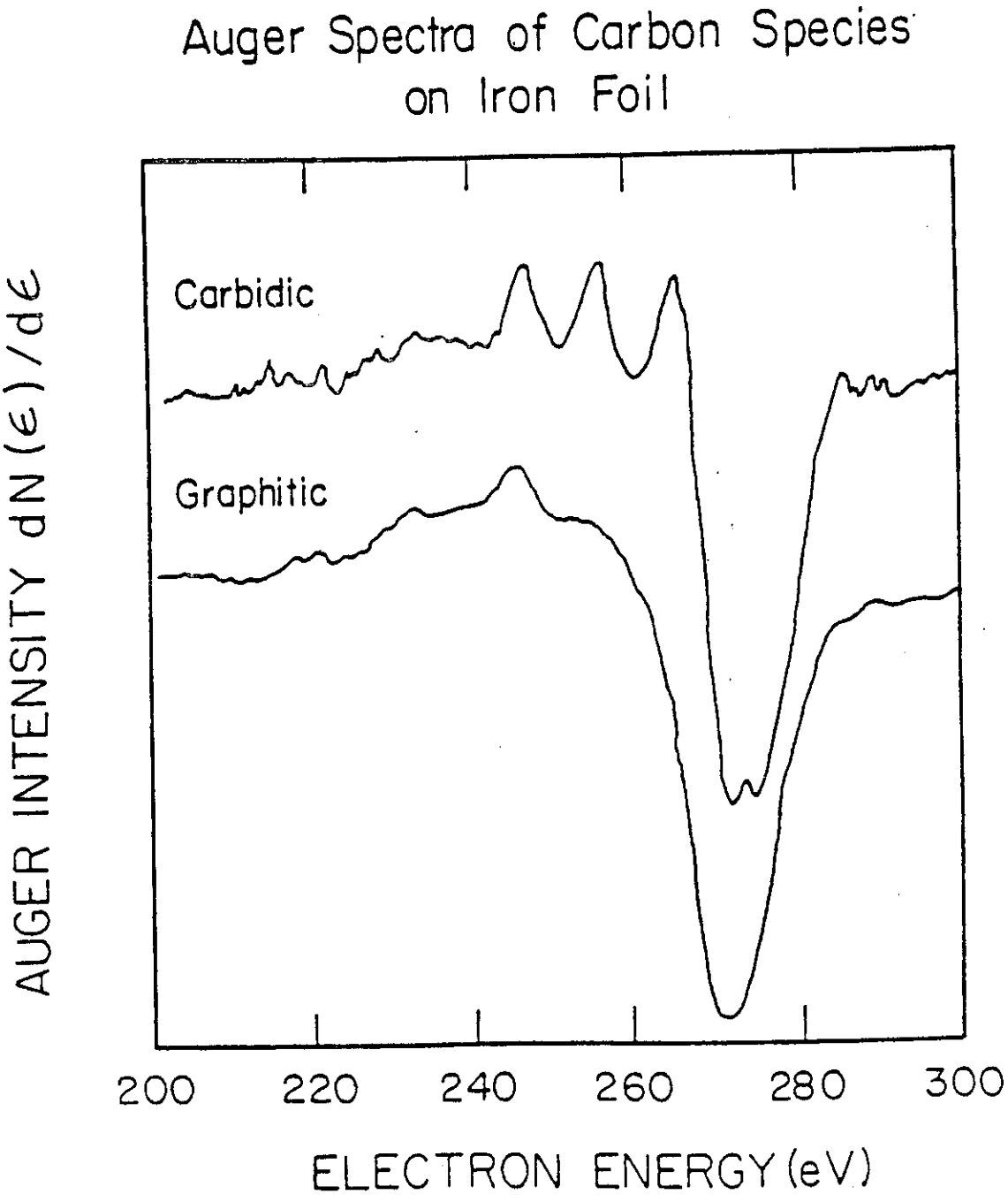


Figure 22

Sample of carbon species found on surface after reactions. Carbidic is an active carbon, while graphitic is relatively inactive to hydrogenation or oxidation.

$CO + H_2$ on clean Mo_{foil}
1 : 2
6 atm

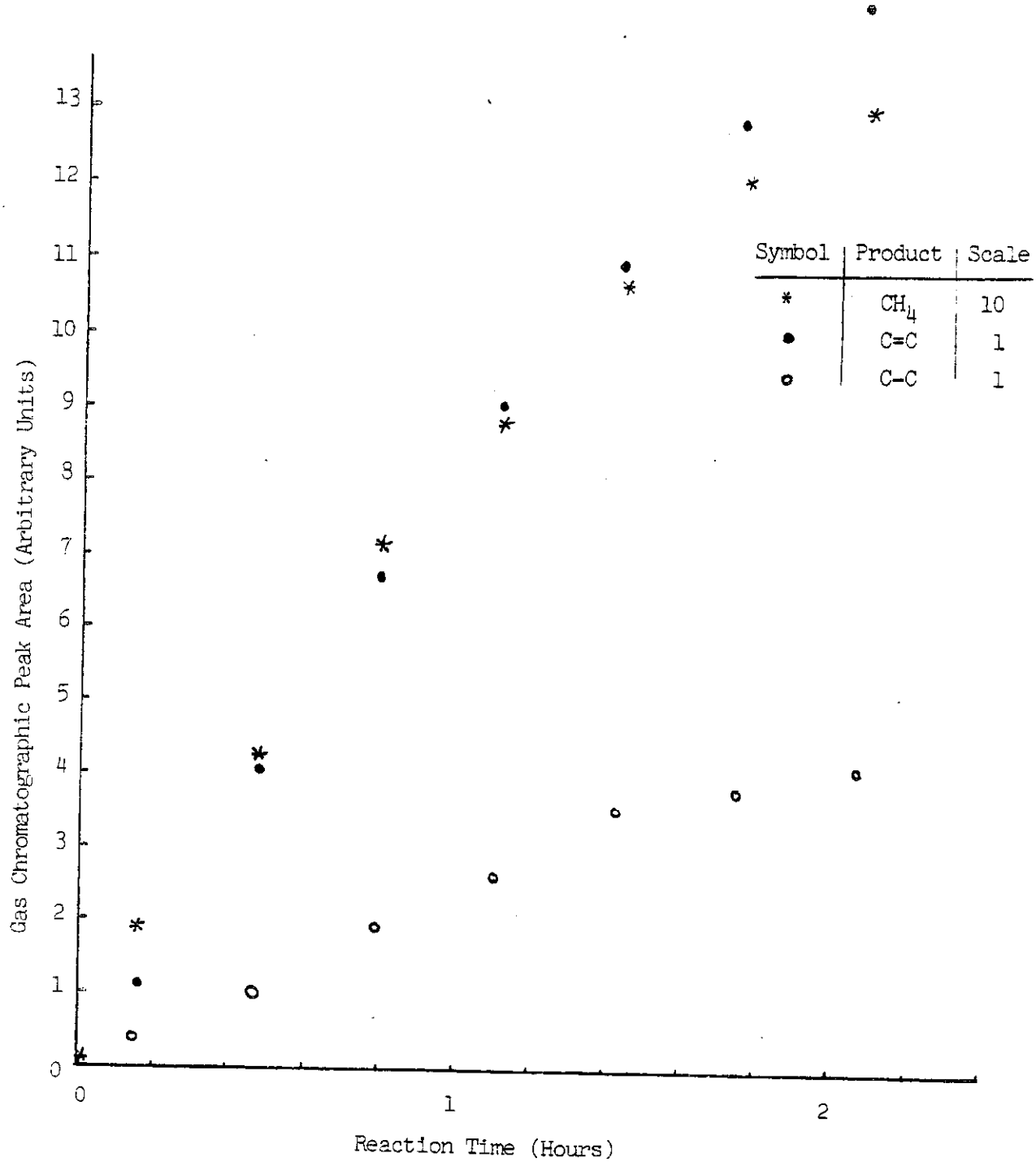


Figure 23
Product Accumulation Curve

$CO + H_2$
1 : 2 300°C
6 atm

Catalyst	Mo_{foil}	Mo+0.25ML K	Rh	Fe(111)
CH_4 Turnover Frequency	0.11	0.15	0.37	1.35

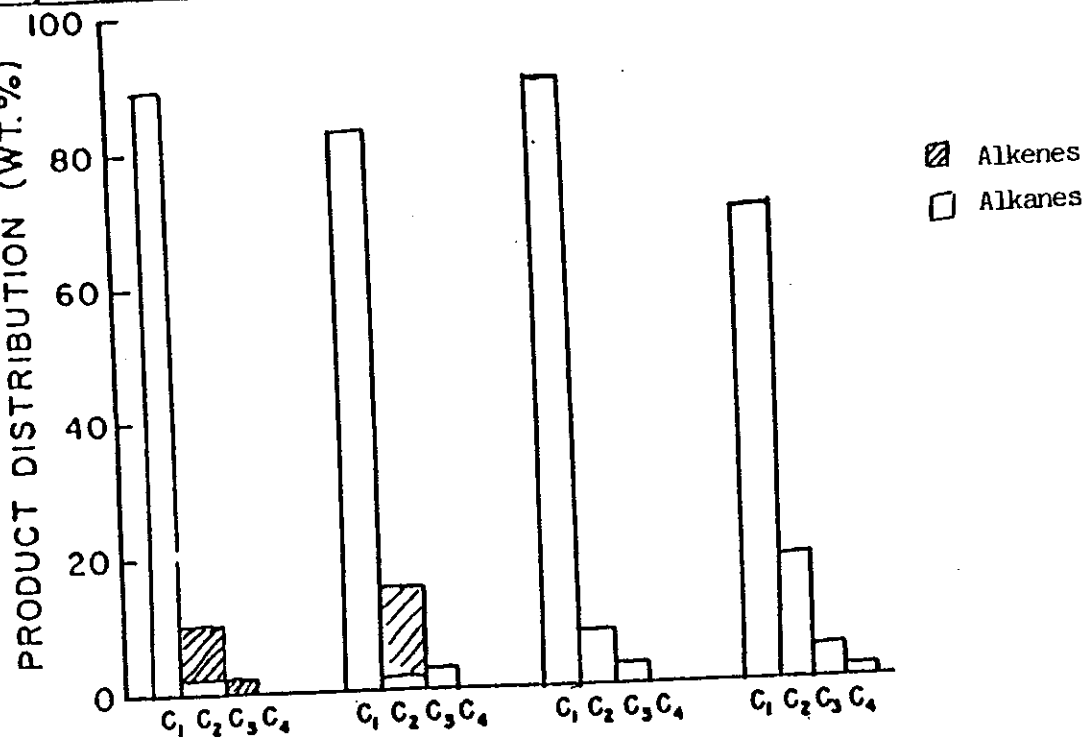


Figure 24

Product Distributions of Several Catalysts for $CO + H_2$

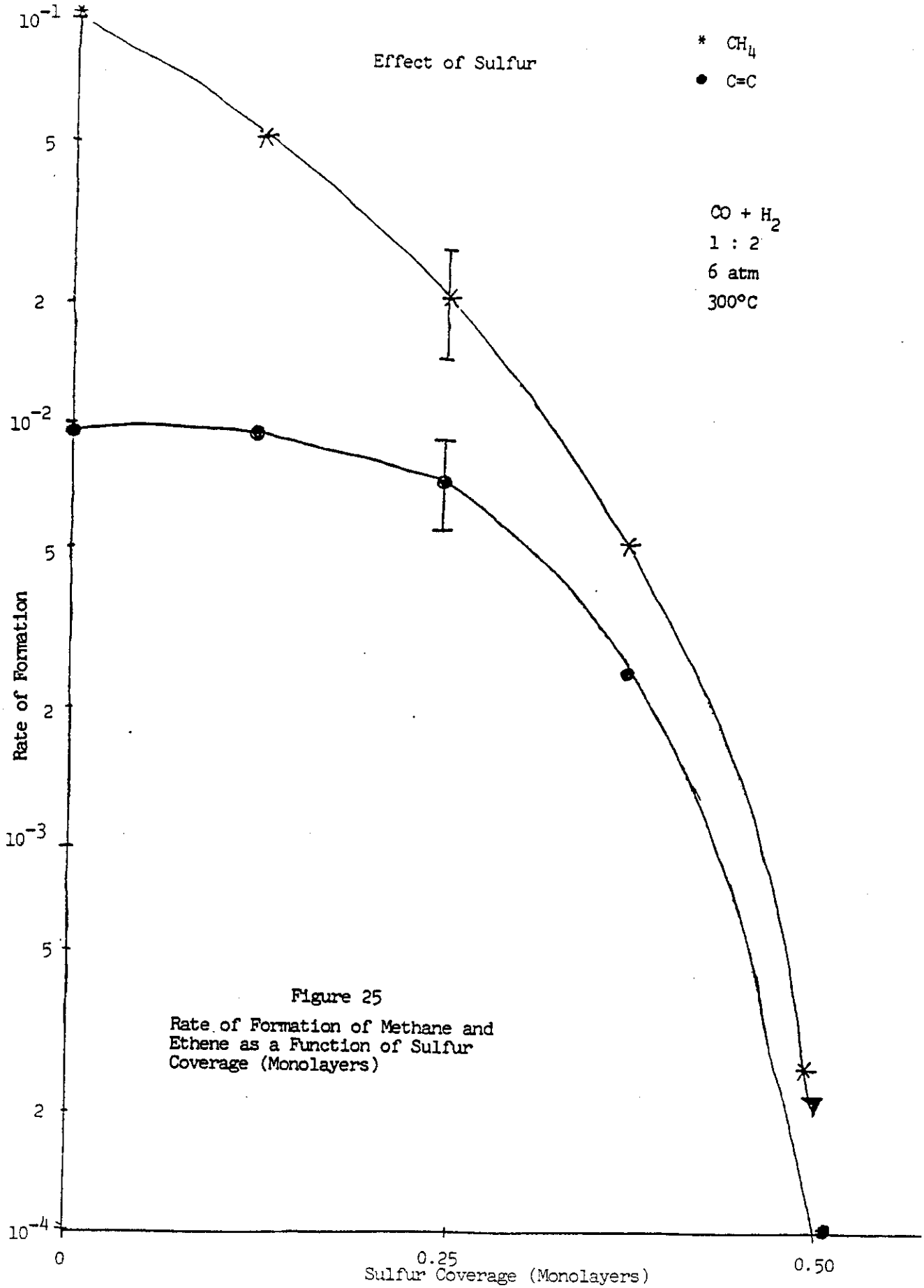


Figure 25

Rate of Formation of Methane and Ethene as a Function of Sulfur Coverage (Monolayers)

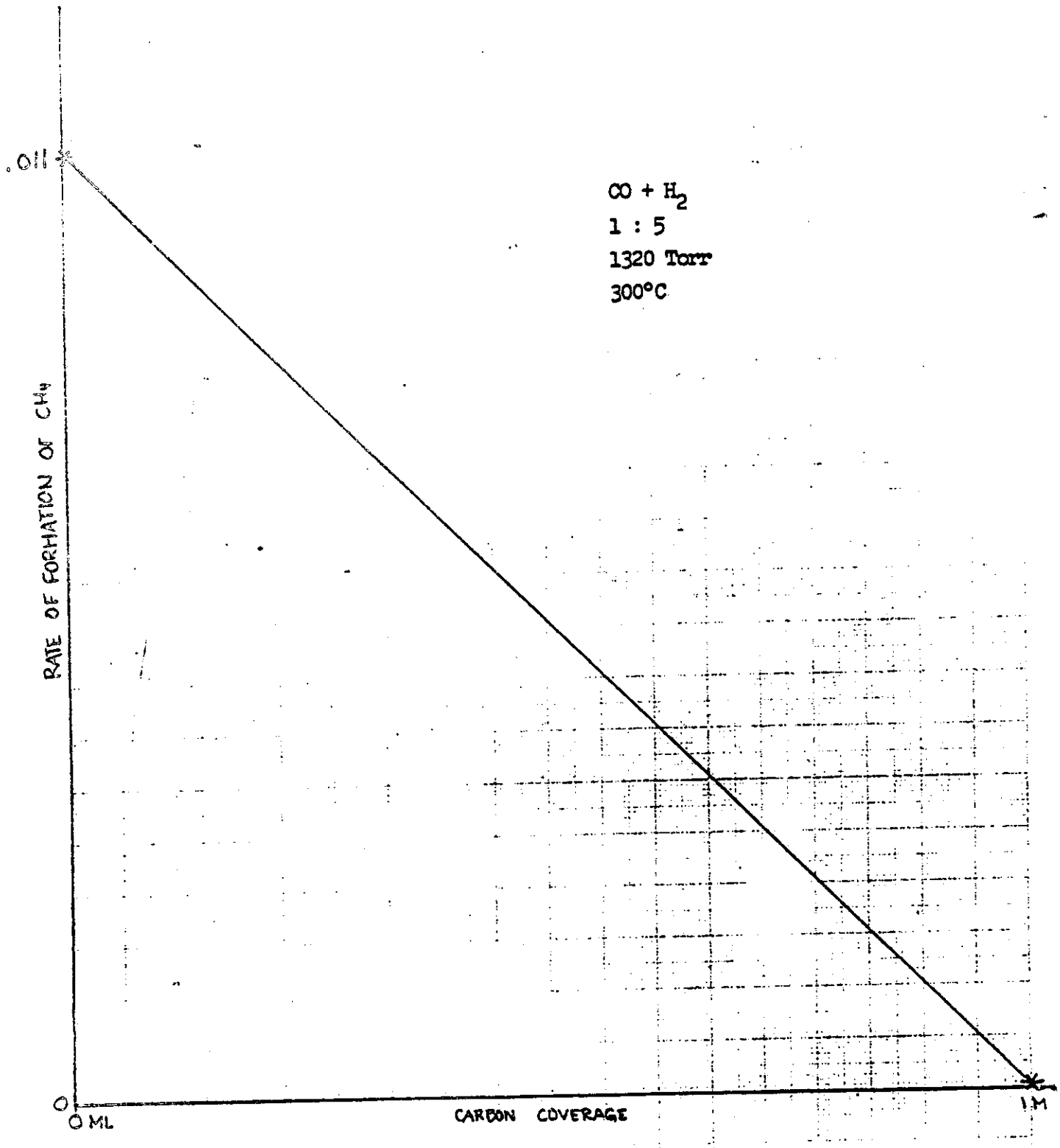


FIG. 26 EFFECT OF SURFACE CARBON ON THE INITIAL RATE OF METHANATION

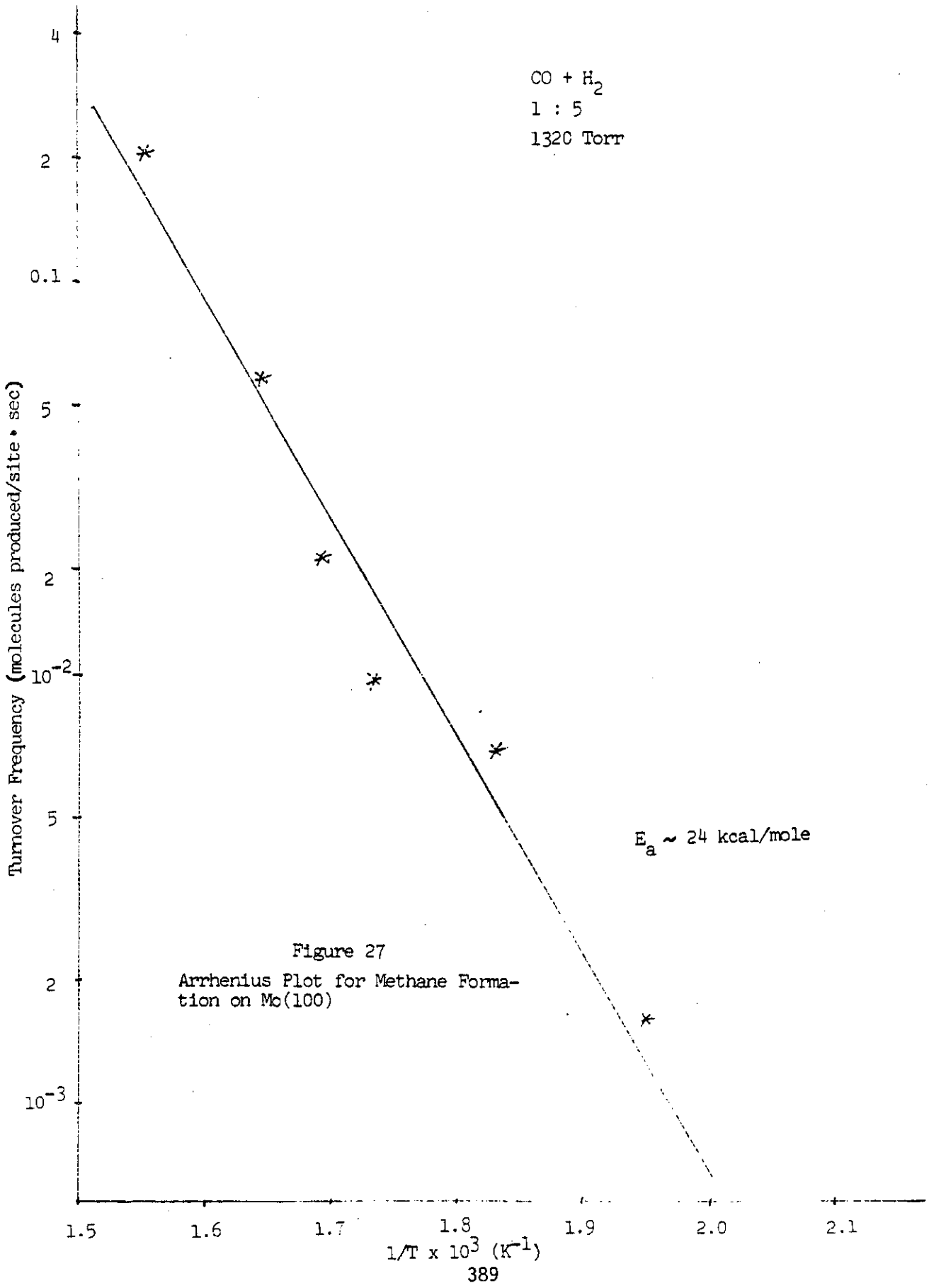


Figure 27

Arrhenius Plot for Methane Formation on Mo(100)

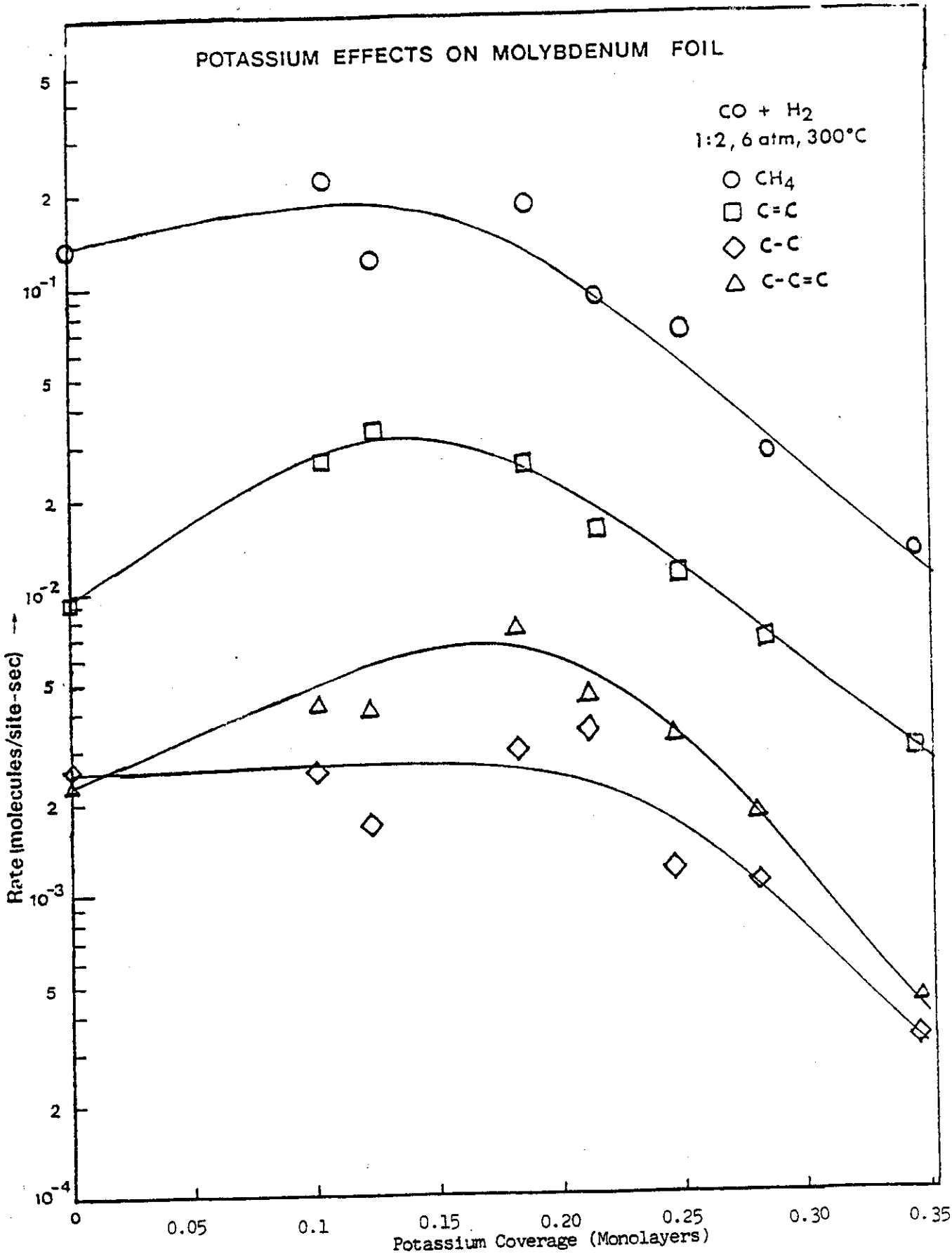


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Figure 28

Effect of Potassium on the Activity and Selectivity of the Hydrogenation of CO on Mo