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D. Dwyer, K. Yoshida, and
G. A. Somorjai

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SYMPOSIUM ON SYNTHESIS GAS CHEMISTRY

PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY

AMERICAN CHEMICAL SOCIETY

ANAHEIM MEETING, MARCH 12-17, 1978

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BY

D. Dwyer, K. Yoshida and G. A. Somorjai*

Mailing Address:

Professor G. A. Somorjai

Department of Chemistry

University of California

Berkeley, California 94720

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D. Dwyer, K. Yoshida and G. A. Somorjai
Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Department of Chemistry, University of California,
Berkeley, California 94720

Abstract

An experimental arrangement consisting of an ultrahigh vacuum bell jar equipped with an internal sample isolation cell was used to investigate the hydrogenation of CO over Fe and Rh surfaces. This apparatus permitted both UHV surface characterization (Auger electron spectroscopy, low-energy electron diffraction) and high pressure (1-20 atm) catalytic reactions to be carried out. Small surface area ($\sim$1 cm^2) metal samples, both single crystals and polycrystalline foils, were used to catalyze the H_2/CO reaction at high pressures (1-6 atm). Reaction products were monitored with a gas chromatograph equipped with a flame ionization detector. The surface compositions of the metal samples were determined before and after the reaction and the results correlated with the observed product distributions and reaction rates. In addition, the influence of various surface additives (carbon, oxygen, potassium) was also investigated.

Iron was the more reactive of the two metals studied and was found to produce C_1-C_5 straight chain hydrocarbons but it poisoned rapidly. The catalytically active surface of both metals was covered with a

carbonaceous monolayer. The carbonaceous monolayer was stable on the rhodium surface and produced C_1-C_4 hydrocarbons at a steady rate even after several hours of reaction. The absolute rates on rhodium samples were, however, substantially lower than those observed for the catalytically active iron samples. Differences in the poisoning characteristics and productsdistributions of the initially clean metal surfaces and the promoted rhodium and iron catalysts indicate the importance of additives and the formation of surface compounds in controlling the activity and selectivity.

Studies of catalyzed reactions of CO and CO_2 with hydrogen to produce hydrocarbons have had a profound effect on the chemical research and chemical technology.[1] As a result of coal gasification (coal + $H_2O \rightarrow CO + H_2$) CO and H_2 are produced and may be utilized as feedstock or as a fuel (water gas). Using the water shift reaction, ($CO + H_2O \rightleftharpoons CO_2 + H_2$) the CO-$H_2$ mixture can be enriched with hydrogen that is desirable in many of the chemical reactions of these two molecules. Table I lists the thermodynamic data for the coal gasification and water shift reactions.

Using various ratios of CO and H_2 the production of hydrocarbons of different types are all thermodynamically feasible. Let us consider the formation of alkanes, alkenes, alcohols according to the reactions.

$$(n + 1)\ H_2 + 2\ n\ CO \rightarrow C_nH_{2n+2} + n\ CO_2 \qquad (1)$$

$$2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O \qquad (2)$$

$$2n\ H_2 + n\ CO \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O) \qquad (3)$$

The standard free energies of formation of the various products as a function of temperature are shown in Figs. 1, 2 and 3. Since these are exothermic reactions, low temperatures favor the formation of the products. However, these reactions are all kinetically limited. (They have low turnover numbers, 10^{-2} to 10 mole/surface atom sec). Therefore higher temperatures in the range of 500 to 700 K are usually employed to optimize the rates of formation of the products. According to the LeChatelier principle, high pressures favor the association reaction that are accompanied by a decrease in the number of moles in the reaction mixture as the product molecules are formed. Thus the formation of higher molecular weight products is more favorable at high pressures. Figures 4 and 5 show that pressures in excess of 20 atm are desirable to produce higher molecular

weight alcohols or benzene. If reactions are carried out at 1 atm for example, the catalyst cannot exhibit its real performance because of thermodynamic limitations. Thus, we must use a high pressure batch or flow reactor capable of carrying out the reactions of CO/H_2 mixtures up to 100 atm.

Chemical reactions that produce methane from CO and H_2 are called methanation reactions. The other reaction that produces a C_1 hydrocarbon yields CH_3OH methanol. All other reactions that produce C_2-C_n hydrocarbons are called the Fischer-Tropsch reaction named after the scientists who developed much of the early CO/H_2 chemistry. In Germany, during the second World War almost all of the gasoline and much of the hydrocarbon chemicals were produced by the Fischer-Tropsch reaction because of the lack of availability of crude oil. Using a cobalt catalyst that was promoted with thorium and potassium oxides (ThO_2 and K_2O) the typical product distribution that was obtained is shown in Table II. Most of the products are straight chain hydrocarbons and the C_4-C_9 fraction that is utilized in gasoline is of low octane number. It is unfortunate that this product distribution is compared with those obtained by the conventional hydrocracking and reforming processes from crude oil since it only reflects our level of understanding of catalytic chemistry of forty years ago. There are several chemical processes that play important roles in the chemical technology presently which use CO and H_2 mixtures to yield selectively the desired products. Methanol can be produced with an excellent yield over a zinc chromate, copper chromate catalysts that exhibit both the necessary hydrogenation and oxidation activities ($CO + 2H_2 \rightarrow CH_3OH$).[2] Recently palladium and platinum were also found to carry out

this reaction, selectively, at high pressures (12 atm).[3] Methane is produced with a relatively high rate, selectively, over nickel catalysts. This process also finds industrial applications ($CO + 3H_2 \rightarrow CH_4 + H_2O$). One of the earliest reactions involving the insertion of CO into a C_n olefin molecule to produce an aldehyde with one greater C_{n+1} carbon number is the so-called hydroformilation or "oxo" reaction.

The oxo reaction is carried out over homogeneous catalysts, rhodium or cobalt carbonyls and is an important industrial process. Recently the production of acetic acid, acid aldehyde and glycol from CO and H_2, over heterogeneous and homogeneous rhodium catalysts have been reported. Straight chain saturated hydrocarbons are not the only molecules that may be produced in the Fischer-Tropsch reaction. There have been early reports of the predominance of isomers among the products using a promoted thorium oxide, ThO_2 catalyst. This process was called the isosynthesis.[1] The typical product distribution yields a large fraction of isobutane. It is interesting to note that at elevated temperatures large concentrations of aromatic molecules over the same promoted ThO_2 catalyst are also produced.

Thus thermodynamic considerations and available experimental evidence indicate that using CO and H_2 mixtures as reactants one should be able to produce, selectively, a very broad range of hydrocarbon molecules that include alcohols, olefins, acids and aromatic molecules. Using the proper catalysts, it should be possible to avoid producing the broad product distribution that is found in the conventional Fischer-Tropsch reaction. To this end we must scrutinize the composition and structure of the active catalyst on the atomic scale and change it, if it is possible,

in a way to control the product distribution and the reaction rate.

Our method of investigation is to correlate the reaction rates and product distributions with the catalyst composition and structure. The apparatus we use for this purpose and the experimental procedures are described below.

Experimental

The apparatus used has been described in detail elsewhere.[4] It consists of a diffusion pumped ultrahigh vacuum bell jar (1×10^{-9} torr) equipped with a retarding grid Auger electron spectroscopy (AES) system, a quadrupole gas analyzer and a 2 keV ion sputter gun. The unique feature of the apparatus is an internal sample isolation cell which operates as a microbatch reactor (100 cc internal volume) in the 1-20 atm pressure range while maintaining UHV in the bell jar. An external gas recirculation loop is attached to the cell through which the reactant gas mixture is admitted. The loop also contains a high pressure bellows pump for gas circulation and a gas sampling valve which diverts a 0.1 ml sample to a gas chromatograph.

The metal samples were approximately 1 cm^2 polycrystalline foils (99.99% pure) or single crystals which were pretreated in a hydrogen furnace (1 atm H_2) at 800°C for 4 days prior to mounting in the vacuum system. This hydrogen treatment was necessary to remove bulk carbon and sulfur impurities which otherwise migrate to the surface during +6 UHV cleaning procedures. The metal samples were mounted such that they could be resistively heated and the temperature was monitored with a chromel-alumel thermocouple spot welded to the sample edge.

The hydrogen and carbon monoxide used to prepare the synthesis gas were of high purity research grade. The mixtures were prepared in the circulation loop then expanded into the isolation cell. Analysis of the synthesis gas by gas chromatography and mass spectrometry indicated that H_2O is very small amounts was the only impurity.

The clean metal surfaces were prepared in ultrahigh vacuum by ion sputtering (Ar^+, 2 keV, 100μA) at high temperatures (800°C) for 15 to 20 minutes, then annealing at 700°C for 2 minutes. The procedure generally produces a surface which was free from sulfur and oxygen. The only detectable surface impurity after this treatment was carbon (10-15% of a monolayer). Once a clean surface was prepared the isolation cell was closed and the synthesis gas admitted into cell at the desired pressure. The sample temperature was then raised to 300°C and gas chromatographic sampling of the reaction products was commenced. At any point in the reaction the cell and circulation loop could be evacuated, the sample cooled to room temperature and then cell opened to UHV to allow AES analysis of the surface. The pump down procedure from 6 atm to 5×10^{-8} torr took approximately 1 minute.

Studies of the Hydrogenation of CO and CO_2 Over Rhodium

Using the high pressure cell, methanation reaction was studied on initially clean polycrystalling rhodium and iron surfaces. The initial experiments were carried out at 1 atm, where methane is expected to be the main product of the reaction. Table III shows the rate, the activation energy and product distribution observed over the small area rhodium surface and compares these values with those found using dispersed alumina supported rhodium catalysts under identical conditions.[5] The results are in excellent agreement. The identity of these experimental data observed over the surfaces of the same metal but widely different surface structure indicates that methanation is likely to be a structure insensitive reaction at 1 atm. Changing the H_2/CO ratio does not markedly affect the product distribution under these conditions as shown in Table IV. Auger electron spectroscopy indicates that during the reaction the active surface is covered with a near monolayer of carbonaceous deposit but oxygen is not detectable on the surface. The reaction may be interrupted and started up again, the surface remains active indefinitely and the monolayer of carbon deposit appears to reflect the surface composition of the active catalyst at a steady state. Oxygen may be readily adsorbed on the surface in the absence of H_2 and CO and it forms ordered surface structures on both (111) and (100) crystal faces of rhodium[6] as shown in Tables V and VI. However the chemisorbed species are removed rapidly by either CO or by hydrogen at low temperatures below the temperature range for the methanation reaction, as CO_2 or H_2O. Figure 7 shows the thermal

desorption of adsorbed oxygen in the presence of CO as CO_2 from the rhodium surface at about 500 K. The rapid rate of reaction of oxygen with both CO and H_2 explains the absence of surface oxygen after the reaction. Yet the pretreatment of the surface with oxygen alters the product distribution for a short period (alcohols and other oxygenated products form) and then the methanation reaction becomes predominant again as its steady state is reached. Pretreatment of the surface with C_2H_2 decreases the rate of methanation markedly. The effects of various pretreatments on the rhodium surface on the rate of methanation and on the product distribution are summarized in Table VII.

The chemisorption of CO on the clean rhodium and on the metal covered with the carbonaceous deposit show interesting changes. Thermal desorption exhibits only one peak as CO desorbed at a fairly low temperature, 570 K. It appears that the rhodium surface adsorbs and retains molecular CO at 300 K. When CO is adsorbed on the carbon-covered rhodium surface two thermal desorption peaks appear, one is identical with the peak from clean rhodium and the other is at a much higher temperature. This latter peak can be associated with dissociated CO that partly recombines and desorbs as a molecule only at about 1000 K. These results indicate that adsorbed CO remains in the molecular state on clean rhodium at 300 K but is effectively dissociated at the same temperature on the carbon covered rhodium surface implying a drastically different chemical bonding on the two types of surfaces. CO forms a series of surface structures on the (111) and (100) crystal faces of rhodium[6] that indicate a contraction of the surface unit cell as the CO surface coverage is increased at higher ambient pressures.

LEED studies of the chemisorption of CO_2 on the rhodium (111) and rhodium (100) surfaces[6] indicate identical behavior to that of CO. The identity of the ordering and structural features imply that CO_2 is dissociated on the rhodium surfaces at 300 K to chemisorbed CO and O and as the oxygen is removed from the surface by another CO molecule as CO_2, the surface chemistry becomes that of chemisorbed pure CO. The methanation reaction when it is carried out using CO_2 instead of CO also clearly reflects this behavior. The CO_2/H_2 mixture produces pure methane, CH_4, and the activation energy for this reaction is 16 kcal/mole as compared to 24/mole using CO and H_2 mixtures. This is shown in Fig. 8. These results can be explained by considering the water shift reaction as a necessary step to convert the arriving CO_2 molecules to CO at the surface first. As a result of the water shift equilibrium the H_2/CO ratio is much larger when starting with CO_2 than the H_2/CO ratio when starting with CO. The higher rates of methanation and the shift of the product distribution toward pure methane are all expected in this circumstance.

Comparison of Rhodium and Iron for the Hydrogenation of CO and CO_2

Both rhodium and iron polycrystalline foils have been used and compared at 6 atm. Again methanation was predominant even at this high pressure range. Iron was found to be a better methanation catalyst than rhodium as indicated by Fig. 9. The distribution of higher molecular weight products from the two metal surfaces are somewhat different as shown in Fig. 10. Iron produces hydrocarbon products up to C_5 under these circumstances. Although the rates of methane formation on iron are higher, the activation energies of the methanation reaction are very similar to those found for rhodium when CO (23 kcal/mole) or when CO_2

(15 kcal/mole) were used as reactants. This implies a similarity of surface chemistry for the formation of CH_4 by the two metals. The active iron surface is also covered with a monolayer of carbon just as rhodium was and one detects no chemisorbed oxygen on the catalyst, by Auger electron spectroscopy. However, the iron surface does not remain active for long in the CO/H_2 mixture, unlike the rhodium surface. After 120 minutes the product distribution changes to pure methane and the rate of reaction slows down markedly while the activation energy drops to 15 kcal/mole. The Auger spectra indicates the build up of a carbon multilayer deposit as this change in reactivity is observed and finally the presence of iron on the surface can no longer be detected. This is shown in Fig. 11. The active iron surface is poisoned rapidly and appears to be unstable under our reaction donditions. The same behavior is observed when using CO_2/H_2 mixtures or when the surface is pretreated with oxygen. The initial activity for methanation is higher in these circumstances and the presence of surface oxygen is detectable at first by Auger spectroscopy. However, after a short period of about 1 hour the surface oxygen disappears and shortly after multilayer carbon deposits form effectively poisoning the iron surface.

Using hydrogen-argon mixtures the multilayer carbon can be removed from the iron surface as methane at a slow rate by the reaction between hydrogen and the surface carbon multilayers. However, the active iron surface appears to be unstable under the same conditions of the methanation reaction where rhodium was stable. Both active surfaces, however, are covered with a monolayer of carbon.

Discussion

Starting with initially clean rhodium and iron surfaces the surface rapidly becomes covered with a monolayer of active carbon. This active carbon layer appears to hydrogenate directly to produce methane by a mechanism which is very similar for both rhodium and iron. While rhodium-carbon monolayer systems remain stable indefinitely under our experimental conditions, the iron-carbon monolayer surface poisons rapidly and multilayer carbon deposits build up.

A series of interesting studies of the methanation reaction have been carried out by Rabo et al using pulsed reactor techniques.[7] CO was adsorbed on nickel, cobalt, ruthenium and palladium dispersed catalyst surfaces at various surface temperatures. The molecule may adsorb intact or it dissociates to carbon and oxygen and then the chemisorbed oxygen is removed with an additional molecule of CO as CO_2 as indicated before. The prerequisite for the disproportion reaction $2CO \rightarrow C + CO_2$ is the weakness of the surface oxygen bond as compared to the carbon-oxygen bond energy in CO_2. Since the appearance of CO_2 is the result of the disproportionation reaction the amount of carbon on the surface can be titrated by the amount of molecular CO_2 that is determined by analysis of the products that appears after CO chemisorption. Once the surface composition is determined and it is known to consist of surface carbon and molecular CO in certain fractional coverages, a pulse of H_2 was admitted at a given surface temperature and the formation of methane and other hydrocarbon products was monitored. It was found that CO dissociates and yields surface carbon on nickel, cobalt and ruthenium surfaces at 600 K while it remains molecular on palladium under these conditions. Pulses of H_2 produce CH_4

efficiently by reaction with this surface carbon. The reaction between surface carbon and hydrogen produces methane even at 300 K. When CO was adsorbed on these surfaces at 300 K it remained largely molecular (as indicated by the absence of CO_2 to evolution). The rate of production of CH_4 from adsorbed molecular CO was undetectable above 300 K but it was detectable and shows at 500 K. It appears that surface carbon produces methane at a higher rate than molecular CO does although the experiment indicates that molecular CO also reacts to form methane at a slow rate. This was proven by the studies using palladium catalyst surfaces that produce methane at a slow rate even though only molecular CO is present on the surface. Thus there are two mechanisms of methanation that can be distinguished involving both active surface carbon and molecular CO. A similar result was obtained by Wise et al.[8] who found CH_4 formation from nickel by only one route by the reaction with the surface carbon. Palladium has not only produced methane at a slow rate although only molecular CO is present on the surface but at 12 atm it produces methanol also very efficiently. Both palladium and platinum show the ability to produce methanol at high pressures. It has been proposed that methanol formation proceeds via the reaction of molecular CO with hydrogen while methanation proceeds via the reaction of surface carbon with hydrogen most efficiently.

The nature of the active carbon monolayer on the transition metal surfaces remains to be explored. On heating to 800 K its activity for methanation is largely lost. Low-energy electron diffraction and Auger electron spectroscopy studies indicate rapid graphitization at these higher temperatures. Thus the bonding of the active carbon (both carbon-

carbon and metal-carbon bonds) must be very different from that of graphite. Perhaps carbene-like metal-carbon bonds are responsible for its hydrogen activity. Using electron spectroscopy and vibrational spectroscopy the properties of this active metal-carbon surface will surely be explored in the near future.

There is a great deal of insight gained into the mechanism of methanation by these and other investigations. There are major differences, however, in the product distribution found on initially clean rhodium and iron catalyst surfaces and on industrial Fischer-Tropsch rhodium and iron catalysts. While rhodium produces oxygenated products and higher molecular weight hydrocarbons on the industrial catalysts, it appears to be a poor but stable methanation catalyst by our investigations. Iron produces larger molecular weight straight chain hydrocarbons and alcohols industrially while it is an unstable methanation catalyst by our studies. It appears that promoters must play an important role in establishing the product distribution. Potassium, calcium and manganese are all used as additives to prepare the active and stable catalyst. It appears that the oxygen surface concentration is one of the important ingredients in controlling the product distribution. Not only will it provide oxygen atoms to be built into the forming hydrocarbon molecules, it may also effectively remove part of the surface carbon, thereby reducing the rate of methanation. Oxygen, however, cannot be added from the gas phase as its reactions with both CO and H_2 are rapid and complete. It must be supplied by adding promoters that want strong metal-oxygen bonds or by forming ternary oxide compounds with part of the metal catalyst. By providing oxygen to the metal by surface diffusion the surface concentration of oxygen may be effectively

controlled. One may write a series of reaction steps that express the findings of methanation and methanol formation studies that both molecular CO and surface carbon that forms by CO dissociation can be hydrogenated to yield the observed products.[10]

Side Reactions

$$CO \rightleftarrows C + O \qquad 2H + O \rightarrow H_2O\uparrow$$

$$H_2 \rightleftarrows 2H \qquad CO + O \rightarrow CO_2\uparrow$$

$$\underbrace{C + H \rightarrow CH + H \rightarrow CH_2 + H \rightarrow CH_3}_{\text{CO insertion, O insertion}} + H \rightarrow CH_4\uparrow$$

CO insertion, O insertion → for chain growth (C_2, $C_3 \ldots C_{11}$ products)

It can be seen that by changing the oxygen surface concentration the equilibrium of the various surface intermediates may be shifted that can also change the product distribution in addition to the possibility of incorporation of oxygen in the product molecules and the removal of the surface carbon by oxygen.

There is much less known about the CO insertion reaction that must be an important step in producing large molecular weight hydrocarbons. There is good evidence for CO insertion into the metal olefin bond using the oxo reaction by the following mechanism

$$HM(CO)_4 \rightleftarrows [HM(CO)_3] + CO$$

$$RCH = CH_2 + [HM(CO_3] \rightleftarrows RCH = CH_2 \downarrow HM(CO)_3$$

$$RCH = CH_2 \rightleftarrows RCH_2CH_2M(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftarrows}} RCH_2CH_2M(CO)_4$$

$$RCH_2CH_2M(CO)_4 \rightleftharpoons RCH_2CH_2COM(CO)_3$$

$$RCH_2CH_2COM(CO)_3 + H_2 \rightleftharpoons RCH_2CH_2\overset{H}{\underset{H}{C}}OM(CO)_3 \rightarrow RCH_2CH_2CHO + [HM(CO)_3]$$

Assuming that olefin intermediates are produced on the surface of the Fischer-Tropsch catalyst similar mechanisms for chain growth have been suggested. Alcoholic intermediates have also been proposed based on the

isotope labeling studies of Emmett et al. on iron surfaces. The understanding and control of the insertion reaction appears to be the key for controlling the product distribution. Clearly the mechanism of this reaction will be subjected to close scrutiny in the near future.

It should be noted that both the surface temperature and the pressure are important variables in this reaction that should be studied independently. Much of the carbon monoxide adsorbed on the catalyst surface at 300 K remain molecular while dissociation commences as the temperature is increased. By changing the surface temperature one can control the ratio of molecular and dissociated carbon monoxide on the surface. Thus low temperature studies are likely to lead to the formation of higher molecular weight hydrocarbons if molecular CO is necessary for the insertion reaction to proceed and carbon is necessary for the methanation reaction to take place. LEED studies indicated that at high pressure the carbon monoxide surface structure undergoes a contraction of the surface unit cell, indicating an enhanced packing of the CO molecules on the surface. Thus the bonding of the carbon monoxide to the surface changes as a function of pressure. Perhaps the pressure has an important influence on the reaction rate and product distribution because of the changing nature of the surface chemical bond between carbon monoxide and the catalyst surface. Another important variable that may be significant in changing the reaction path is the contact time or residence time of the intermediates and reactants on the surface. The CO dehydrogenation reaction is relatively slow indicating a relatively long residence time on the surface. By arranging the reaction conditions so that the contact time is made shorter or longer, the product distribution may be altered. By controlling the contact time,

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equilibrium among the various surface intermediates may be established or may be prevented. Thus the reaction mechanism may be markedly changed as a function of residence time control of the different surface intermediates.

Acknowledgment

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References

1. (a) J. H. Storch, N. Golumbic and R. B. Anderson, The Fischer-Tropsch and Related Syntheses (Wiley, New York, 1951); (b) H. Pickler, Adv. Catalysis 4, 271 (1952); (c) F. Fischer and H. Tropsch, Brennstoff-Chem. 7, 97 (1926).
2. K. Klier, Methanol and Methyl Fuels From Sungas, paper presented at University Contractors Conference ERDA, NSF, RANN, EPRI, Park City, Utah, October 1975.
3. M. L. Poutsma, L. F. Elek, P. A. Ibarbia and J. A. Rabo, to be published.
4. B. A. Sexton and G. A. Somorjai, J. Catalysis 46, 167 (1977).
5. M. A. Vannice, J. Catalysis 37, 449 (1975).
6. D. G. Castner, B. A. Sexton and G. A. Somorjai, Surf. Sci. in press.
7. J. A. Rabo, A. P. Risch and M. L. Poutsma, to be published.
8. P. R. Wenticek, B. J. Wood and H. Wise, J. Catalysis, 43, 363 (1976).
9. R. B. Anderson in Catalysis, (P. H. Emmett, Ed.), Vol IV, (Reinhold, New York, 1956).
10. P. C. Ellgen, W. J. Bartley, M. M. Bhasin and T. P. Wilson, to be published.

Table I

TYPICAL VALUES OF COMMERCIAL-SCALE SYNTHESES ON COBALT CATALYST

Constituent	Wt % of total products listed[a]	Olefins, vol %	Number carbon atoms	Octane number, research method
		Normal-pressure synthesis[b]		
gasol ($C_3 + C_4$)	12	50	$C_3 + C_4$	
gasoline, to 185°C	49	37	C_4-C_{10}	52
gasoline, to 200°C	54	34	C_4-C_{11}	49
diesel oil, 185-320°C	29	15	C_{11}-C_{18}	
diesel oil, 200-320°C	24	13	C_{12}-C_{19}	
soft paraffins, 320-450°C	7	iodine value, 2	>C_{19}	
hard paraffins, >450°C				
		Medium-pressure synthesis[c]		
gasol ($C_3 + C_4$)		30	66% C_4 33% C_3	
gasoline, to 185°C	35	20	C_4-C_{10}	28
gasoline, to 200°C	40	18	C_4-C_{11}	25
diesel oil, 185-320°C	35	10	C_{11}-C_{18}	
diesel oil, 200-320°C	35	8	C_{12}-C_{19}	
soft paraffins, 320°C	30	iodine value, 2	C_{18}	
soft paraffins, 330°C	25		C_{19}	

[a]Total yield per cubic meter of synthesis gas: normal-pressure synthesis, 148 g; medium-pressure synthesis, 145 g of liquid products and 10 g gasol.
[b]At 1 atm; 180-195°C; catalyst, 100Co:5ThO_2:7.5MgO:200 kieselguhr; 1CO:2H_2 (18-20% inert components); throughput 1 m^3 synthesis gas/hr) (kgCo); two stage; no recycle.
[c]At 7 atm, abs; 175-195°C; catalyst, 100Co:5ThO_2:7.5MgO:200 kieselguhr;1CO:2H_2 (18-20% inert components); throughput 1 m^3 synthesis gas/(hr) (kgCo); two stage; no recycle.

Table II

Water Gas Reaction

$$C(graphite) + H_2O \rightleftarrows CO + H_2$$

$$\Delta H_{500K} = +32.0 \text{ kcals mole}^{-1}$$

$$\Delta G_{500K} = +15.2 \text{ kcals mole}^{-1}$$

$$\Delta G_{1000K} = -1.9 \text{ kcals mole}^{-1}$$

Shift Reaction

$$CO + H_2 \rightleftarrows CO_2 + H_2$$

$$\Delta H_{500K} = -9.5 \text{ kcals mole}^{-1}$$

$$\Delta G_{500K} = -4.8 \text{ kcals mole}^{-1}$$

$$\Delta G_{1000K} = -0.6 \text{ kcals mole}^{-1}$$

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Table III

Table III. Comparison of polycrystalline Rh foil with a 1% Rh/Al_2O_3 catalyst in the $CO-H_2$ reaction at atmospheric pressure.

	polycrystalline Rh foil (this work)	supported 1% Rh/Al_2O_3 (Vannice)[7]
Reaction Conditions	300°C, 3:1 H_2/CO 700 Torr	300°C* 3:1 H_2/CO 760 Torr
Type of reactor	batch	flow
conversion	< 0.1%	< 5%
Product Distribution	90% CH_4 ±3 5% C_2H_4 ±1 2% C_2H_6 ±1 3% C_3H_8 ±1 <1% C_4 +	90% CH_4 8% C_2H_6 2% C_3 <1% C_4 +
Absolute Methanation Rate at 300°C (Turnover No.)	0.13±0.03 molecules $site^{-1}$ sec^{-1}	.034 molecules $site^{-1}$ sec^{-1}

*data adjusted from 275°C

Table IV

Surface structures of chemisorbed small molecules of the (100) surfaces of Rh, Pd, Ni, Ir and Pt.

GAS	Rh(100)	Pd(100)	Ni(100)	Ir(100) (1x1)	Ir(100) (5x1)	Pt(100) (1x1)	Pt(100) (5x20)
H_2	(1x1) or disordered		disordered		(5x1) or disordered	(1x1) or disordered	(5x20) or disordered
O_2	(2x2) C(2x2)		(2x2) C(2x2)	(2x1)	(2x1)	(1x1)	not adsorbed
CO	C(2x2) split (2x1)	C(4x2) R45° compressed C(4x2) R45°	C(2x2) "hexagonal"	C(2x2)	(2x2) (1x1)	C(2x2) (1x1)	(1x1) C(4x2)[46] (2x2)
CO_2	C(2x2) split (2x1)			C(2x2) (7x20)	(2x2)		
NO	C(2x2)				(1x1)		(1x1)
C_2H_4	C(2x2)		C(2x2)	(1x1)	(1x1)		C(2x2)
C_2H_2	C(2x2)		C(2x2)	(1x1)	(1x1)		C(2x2)
C	C(2x2) graphite rings		"quasi" C(2x2) graphite rings (2x2) ($\sqrt{7}$x$\sqrt{7}$) R19°		C(2x2)		graphite rings

Table V

Surface structures of chemisorbed small molecules on the (111) surfaces of Rh, Pd, Ni, Ir and Pt and the (001) surface of Ru.

Gas	Rh(111) (This paper)	Pd(111)	Ni(111)	Ir(111)	Pt(111)	Ru(001)
H_2	(1x1) or disordered	(1x1)	disordered (2x2)	(1x1) or disordered	(1x1)	
O_2	(2x2)	(2x2) ($\sqrt{3}$x$\sqrt{3}$) R30°	(2x2) ($\sqrt{3}$x$\sqrt{3}$) R30°	(2x2)	(2x2)	(2x2)
CO	($\sqrt{3}$x$\sqrt{3}$) R30° split (2x2) (2x2)	($\sqrt{3}$x$\sqrt{3}$) R30° C(4x2) split (2x2)	($\sqrt{3}$x$\sqrt{3}$) R30° C(4x2) ($\sqrt{7}$/2x$\sqrt{7}$/2) R19.1°	($\sqrt{3}$x$\sqrt{3}$) R30° (2$\sqrt{3}$x2$\sqrt{3}$) R30° split (2$\sqrt{3}$x2$\sqrt{3}$) R30°	($\sqrt{3}$x$\sqrt{3}$) R30° C(4x2) "hexagonal"	($\sqrt{3}$x$\sqrt{3}$) R30° (2x2) disorder
CO_2	($\sqrt{3}$x$\sqrt{3}$) R30° split (2x2) (2x2)		(2x2) (2x$\sqrt{3}$)			($\sqrt{3}$x$\sqrt{3}$) R30° (2x2)
NO	C(4x2) (2x2)	C(4x2) "star" structure (2x2)	C(4x2) "hexagonal"	(2x2)[52]		
C_2H_4	C(4x2)		(2x2)	($\sqrt{3}$x$\sqrt{3}$) R30°	(2x2)	
C_2H_2	C(4x2)		(2x2)	($\sqrt{3}$x$\sqrt{3}$) R30°	(2x2)	
C	(8x8) (2x2) R30° ($\sqrt{19}$x$\sqrt{19}$) R23.4° (2$\sqrt{3}$x2$\sqrt{3}$) R30° (12x12)		(1x1) ($\sqrt{39}$x$\sqrt{39}$)	(9x9)	graphite rings	(12x12)

Table VI

Variation of reaction product distribution with H_2/CO Ratio and Temperature, over Rh foils.

C_1 = methane $C_2(=)$ ethylene C_2 ethane C_3 propane

Temp.	Product	H_2/CO = 1:2	H_2/CO = 3:1	H_2/CO = 9:1
250°C	C_1	65%	84%	93%
	$C_2(=)$	16	9	4
	C_2	9.8	3	2
	C_3 +	9.2	4	1
300°C	C_1	77%	89%	95%
	$C_2(=)$	13	7	2
	C_2	4	2	2
	C_3+	6	3	1
350°C	C_1	83%	94%	98%
	$C_2(=)$	12	3	0
	C_2	1	2	2
	C_3+	4	1	0.2

Table VII

Variation in methanation activity, and product distributions for the $CO-H_2$ and CO_2-H_2 reactions on clean and pretreated rhodium surfaces. (Reaction conditions 1:3 ratio, 700 Torr, 300°C)

Reaction Gases	Surface Pretreatment*	Methanation Rate (300°C) (turnover number)	Product Distribution
$CO-H_2$	none	0.15±.05	88% C_1 9% C_2 3% C_3
CO_2-H_2	none	0.33±.05	100% C_1
$CO-H_2$	O_2	0.33±.05	87% C_1 10% C_2 3% C_3
CO_2-H_2	O_2	1.7±0.2	98% C_1 2% C_2
$CO-H_2$	CO	0.15±.05	88% C_1 9% C_2 3% C_3
CO_2-H_2	CO	0.33±.05	100% C_1
$CO-H_2$	C_2H_2	.07±.02	78% C_1 18% C_2 4% C_3
CO_2-H_2	C_2H_2	.07±.04	96% C_1 3% C_2 1% C_3

*Heated for 15 mins in 700 Torr of the particular gas, then thermally desorbed to 1000°C in vacuo before reaction.

Figure Captions

Fig. 1 Temperature dependence of the free energy of formation of alkanes from H_2 and CO.

Fig. 2 Temperature dependence of the free energy of formation of alkenes from H_2 and CO.

Fig. 3 Temperature dependence of the free energy of formation of alcohols from H_2 and CO.

Fig. 4 Pressure dependence of the precent conversion of CO and H_2 to benzene.

Fig. 5 Pressure dependence of the precent conversion of CO and H_2 to alcohols.

Fig. 6 Schematic of UHV surface analysis system equipped with sample isolation cell for high pressure (1-20 atm) catalytic studies.

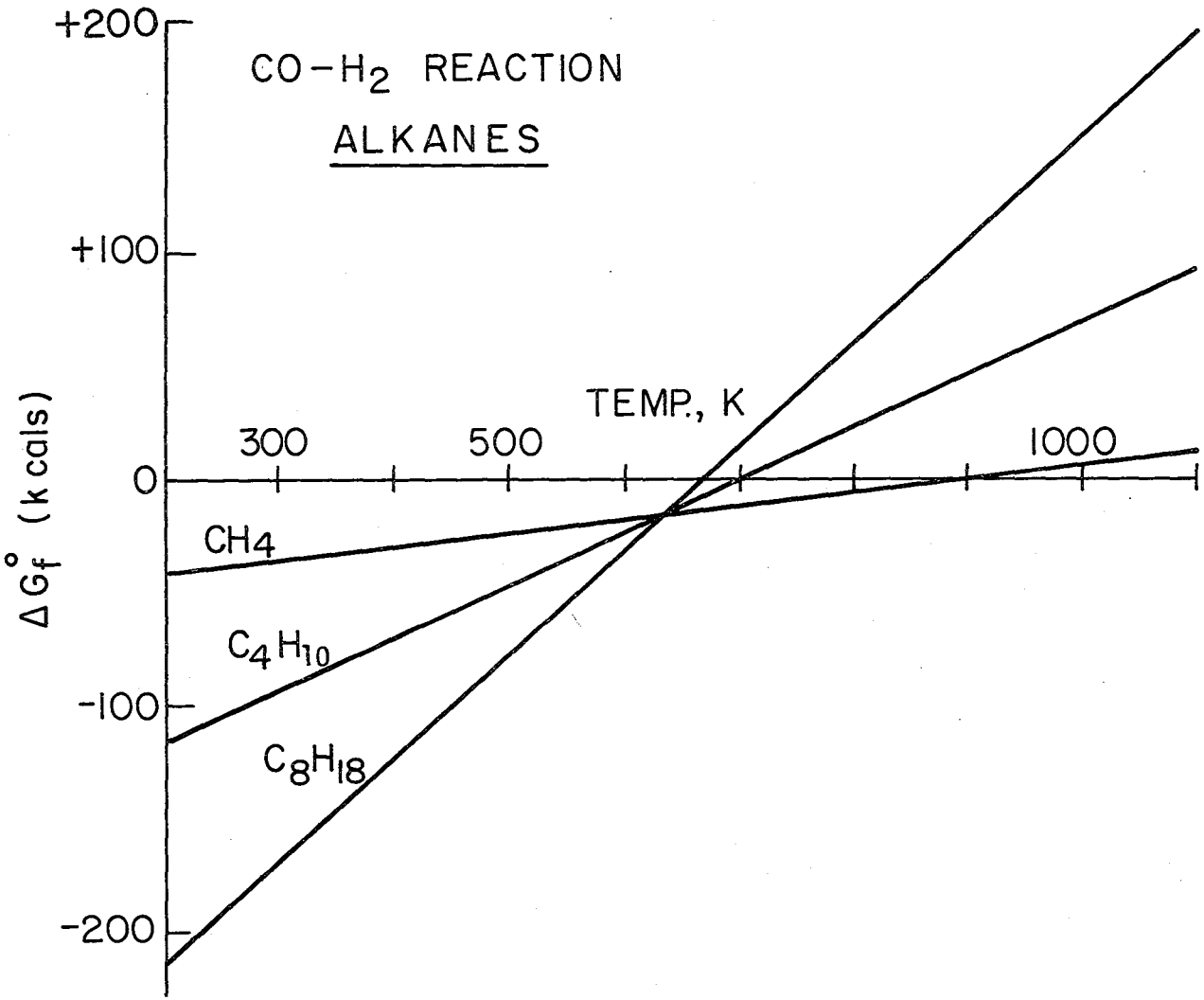
Fig. 7 Thermal desorption of CO_2 from Rh foil after exposure for chemisorbed O_2 and CO.

Fig. 8 Arrhenius plots for methane production from[a] CO_2-H_2 and[b] CO-H_2 mixtures (1:3 ratio, 250-400°C, 700 torr).

Fig. 9 Total accumulation of methane as a function of reaction time over initially clean rhodium and iron foils.

Fig. 10 Comparison of product distributions obtained over initially clean polycrystalline iron and rhodium foils.

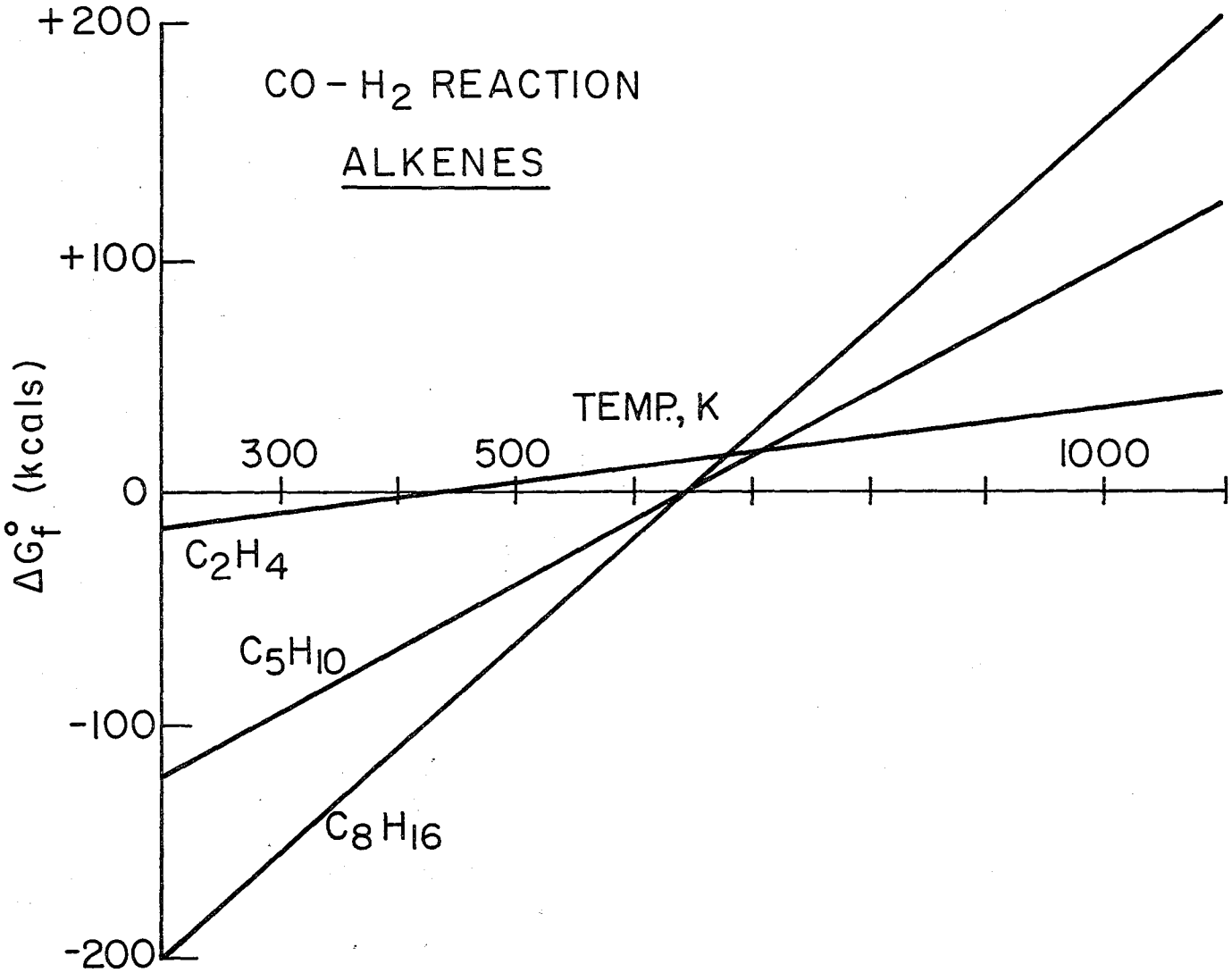
Fig. 11 Aguer spectra of the iron surface before, after 30 minutes and after 4 hours of reaction (6 atm, 3:1 H_2:CO, 300°CO.



XBL 762-591

Fig. 1

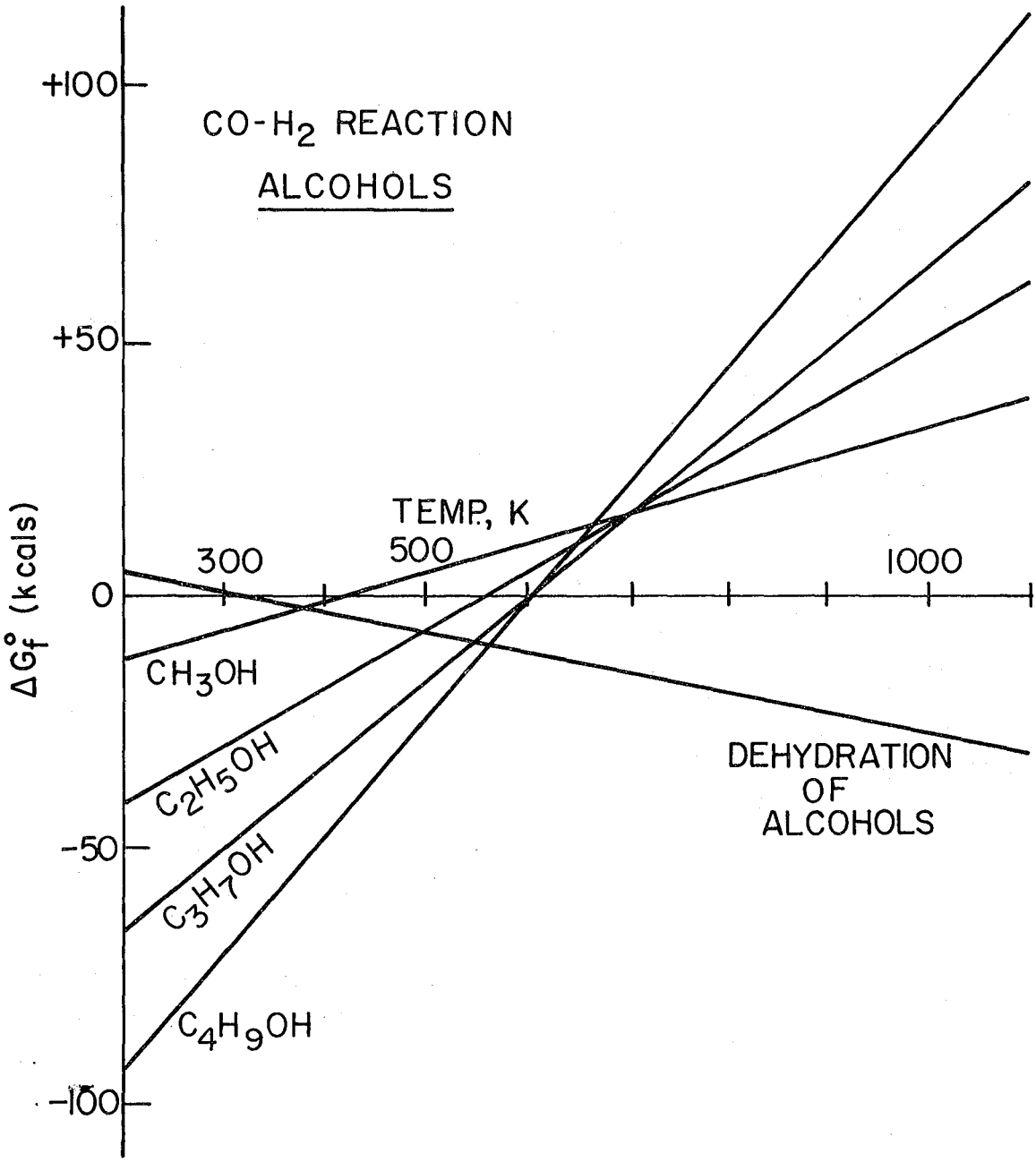
0 0 0 4 9 0 3 5 7 7



XBL 762-592

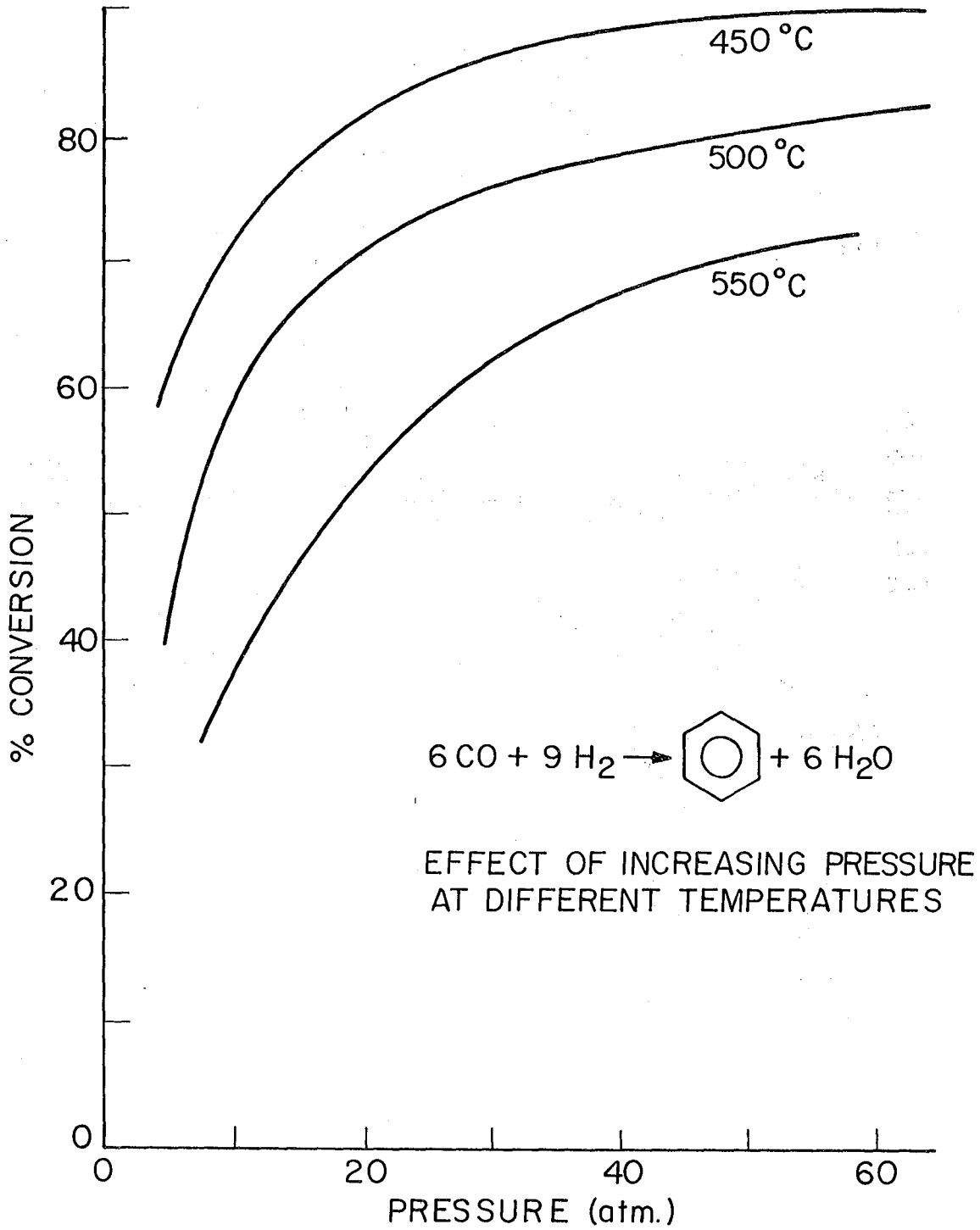
Fig. 2

0 0 0 0 4 9 0 3 5 7 8



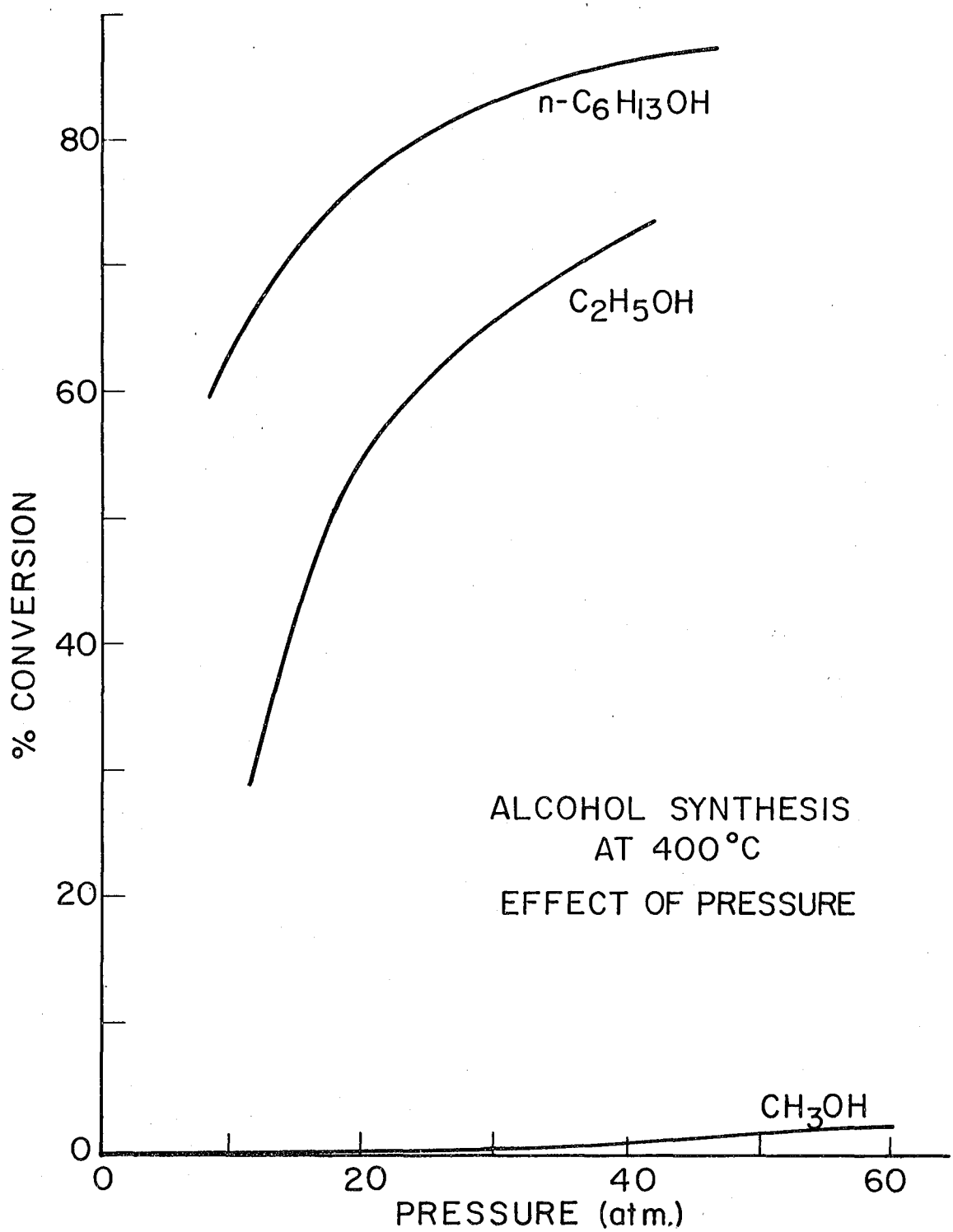
XBL 762-593

Fig 3



XBL 762-590

Fig 4



XBL 762-594

Fig 5

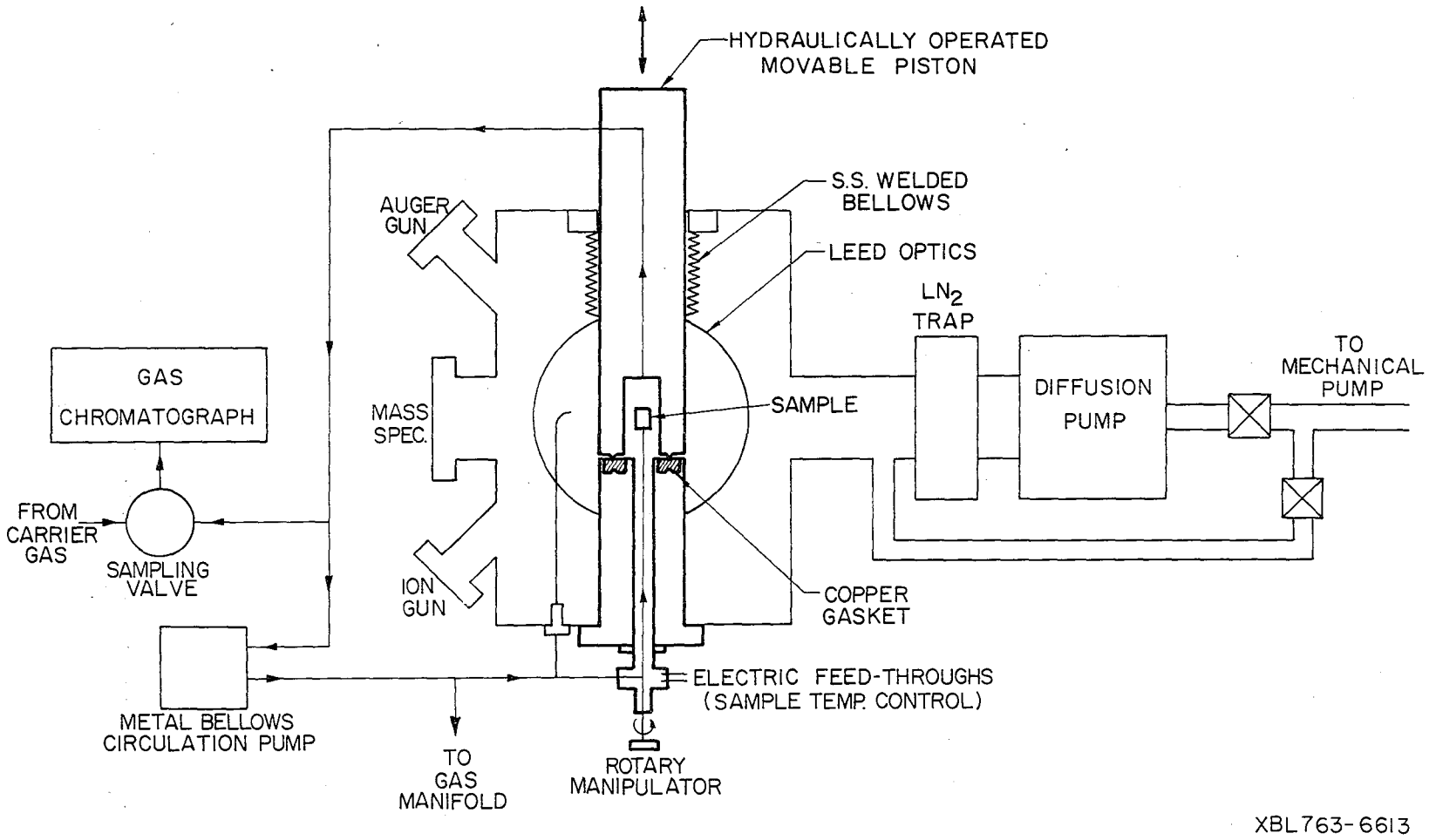
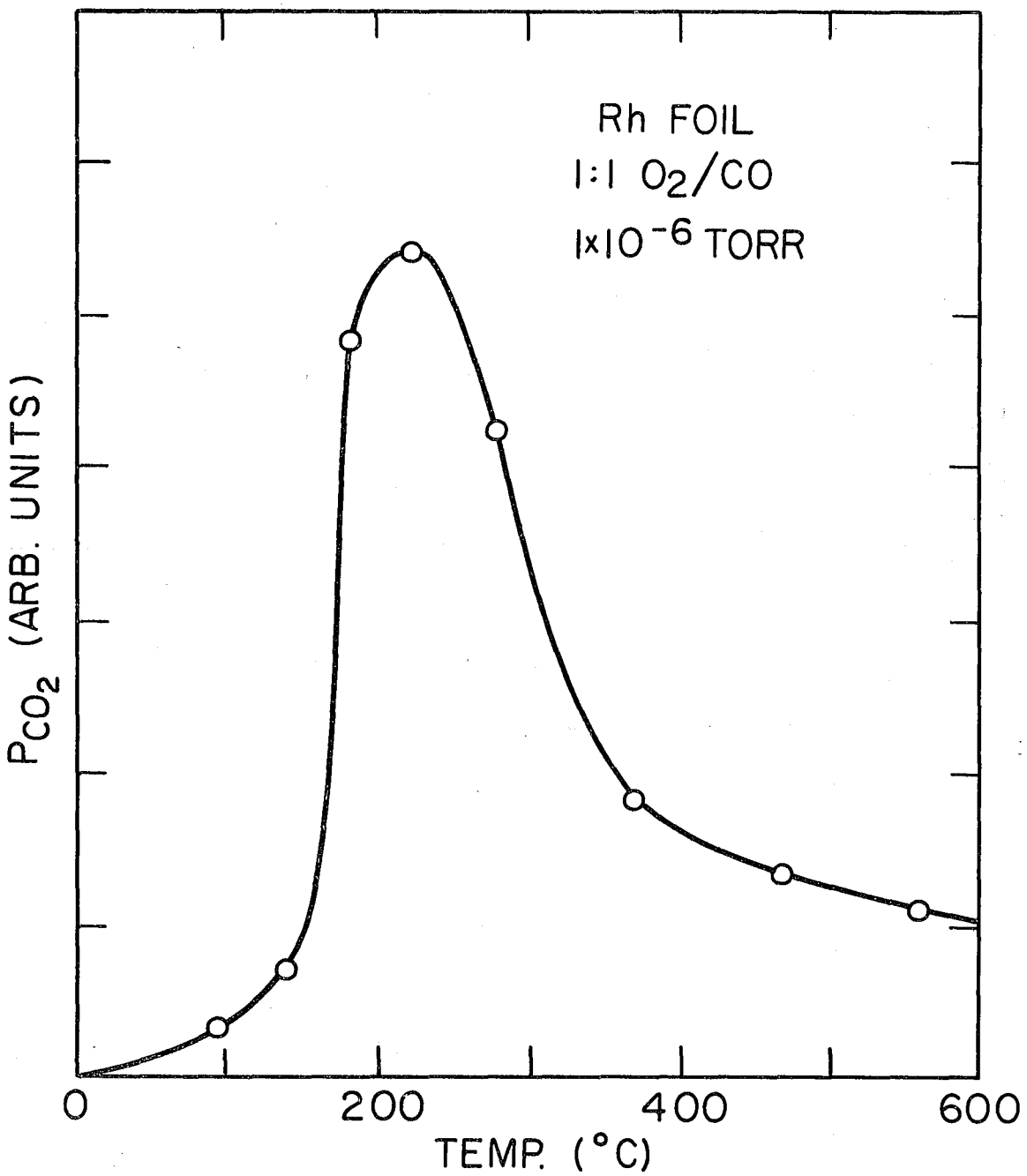
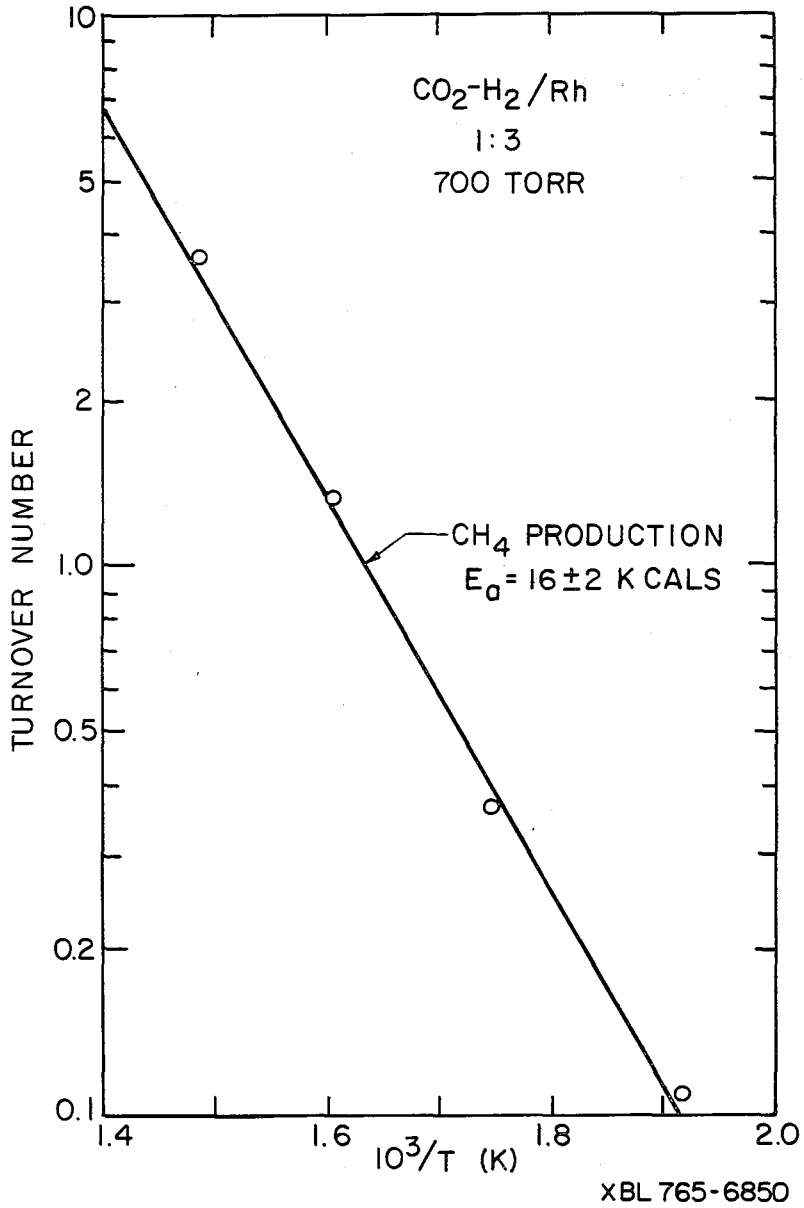

HYDRAULICALLY OPERATED
MOVABLE PISTON
S.S. WELDED
BELLOWS
LEED OPTICS
AUGER
GUN
LN_2
TRAP
GAS
CHROMATOGRAPH
MASS
SPEC.
SAMPLE
DIFFUSION
PUMP
TO
MECHANICAL
PUMP
FROM
CARRIER
GAS
SAMPLING
VALVE
ION
GUN
COPPER
GASKET
ELECTRIC FEED-THROUGHS
(SAMPLE TEMP. CONTROL)
METAL BELLOWS
CIRCULATION PUMP
TO
GAS
MANIFOLD
ROTARY
MANIPULATOR
XBL763-6613

Fig. 6



XBL 765-6841

Fig 7


CO_2-H_2/Rh
1:3
700 TORR
CH_4 PRODUCTION
E_a= 16±2 K CALS
TURNOVER NUMBER
10
5
2
1.0
0.5
0.2
0.1
1.4
1.6
1.8
2.0
$10^3/T$ (K)
XBL 765-6850

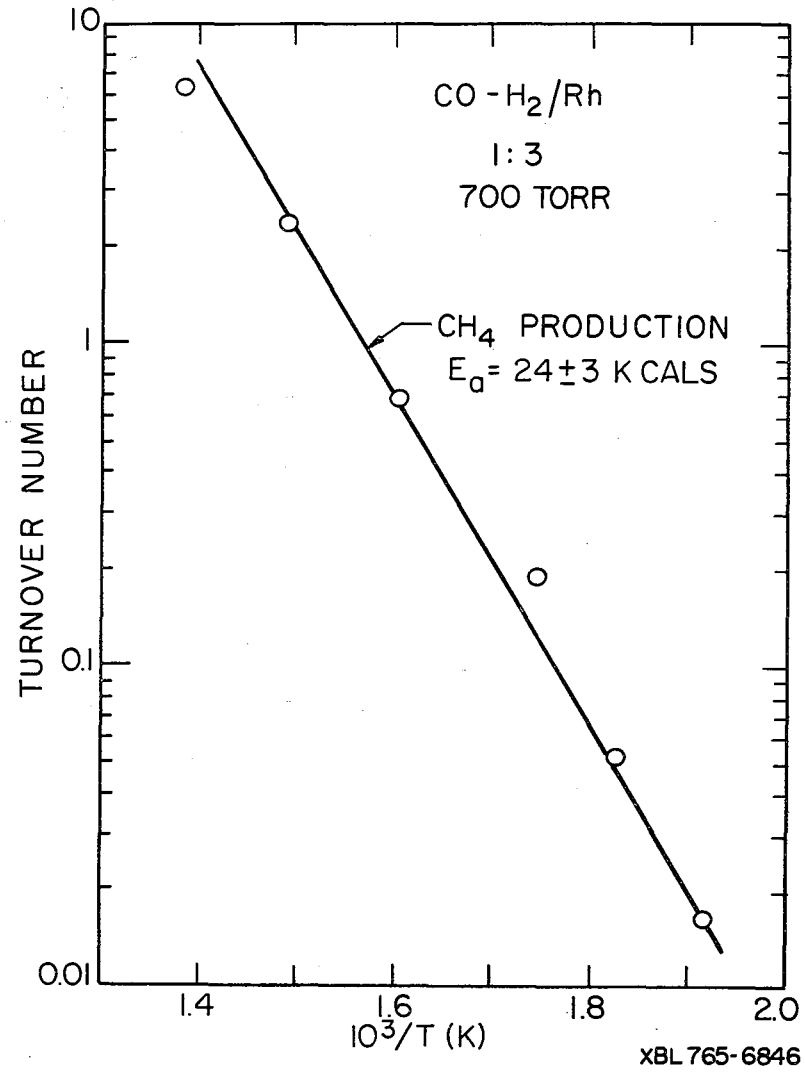
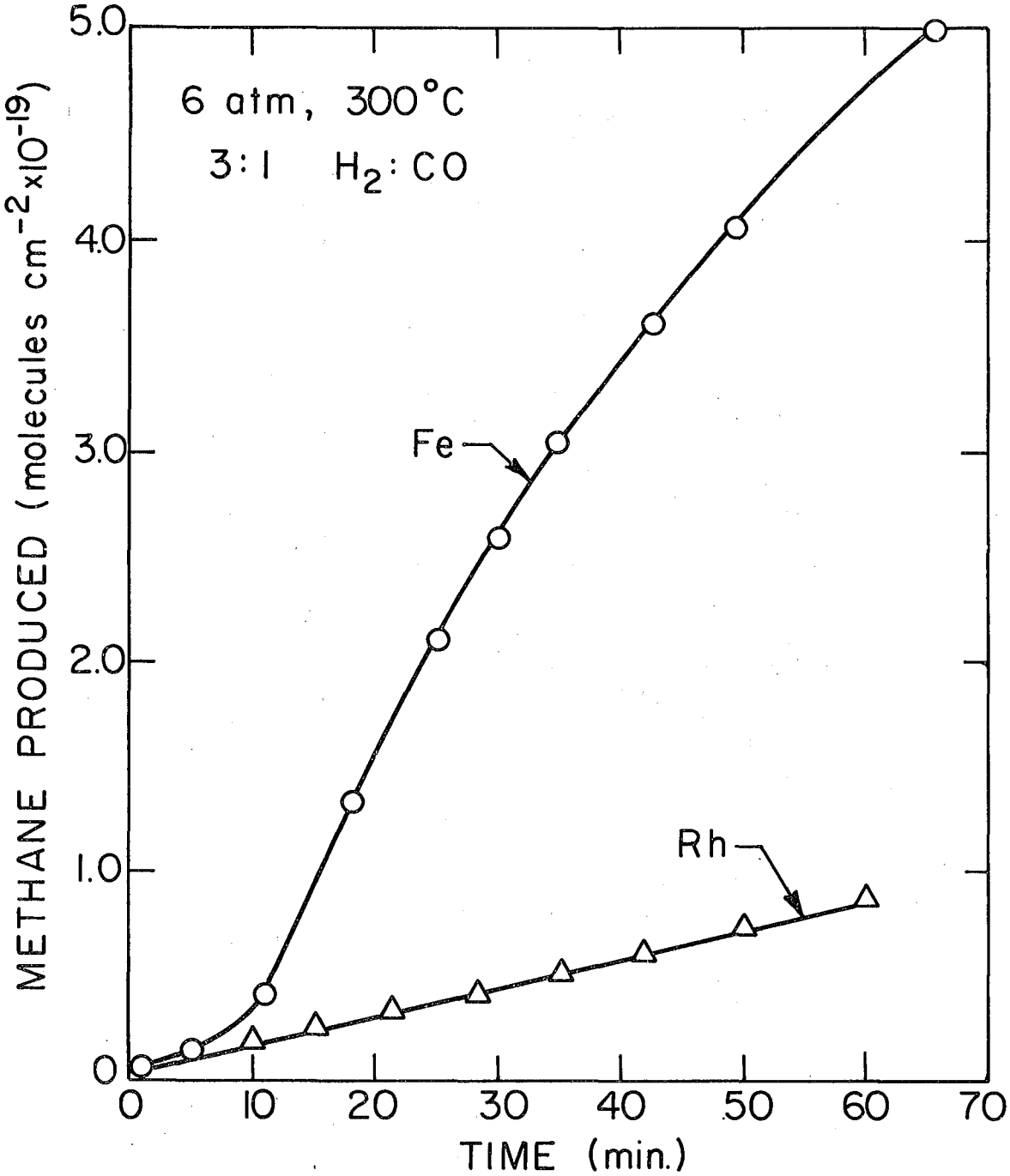

CO - H_2/Rh
1:3
700 TORR
CH_4 PRODUCTION
E_a= 24±3 K CALS
TURNOVER NUMBER
10
1
0.1
0.01
1.4
1.6
1.8
2.0
$10^3/T$ (K)
XBL 765-6846

Fig 8



XBL773-5207

Fig 9

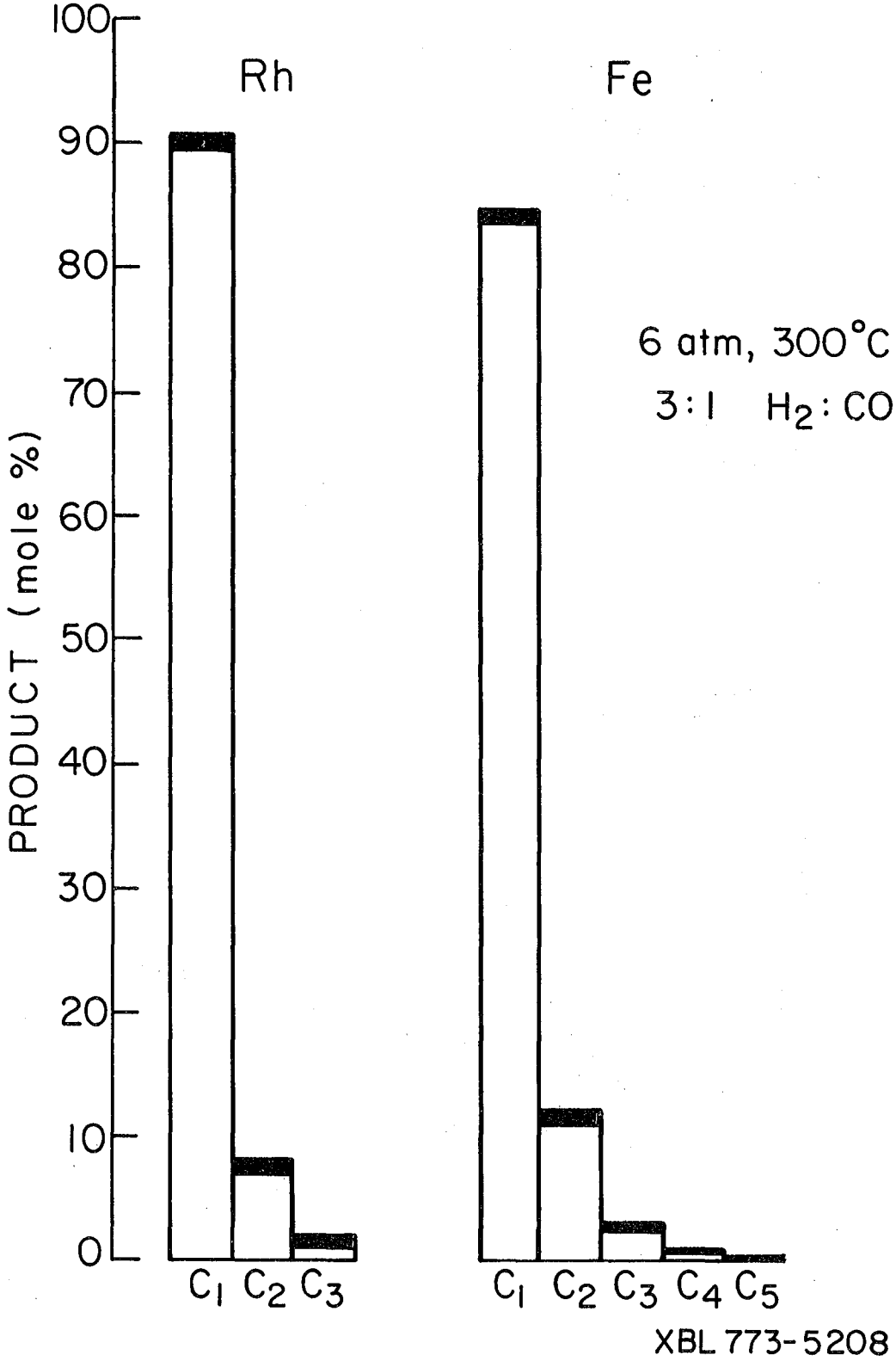
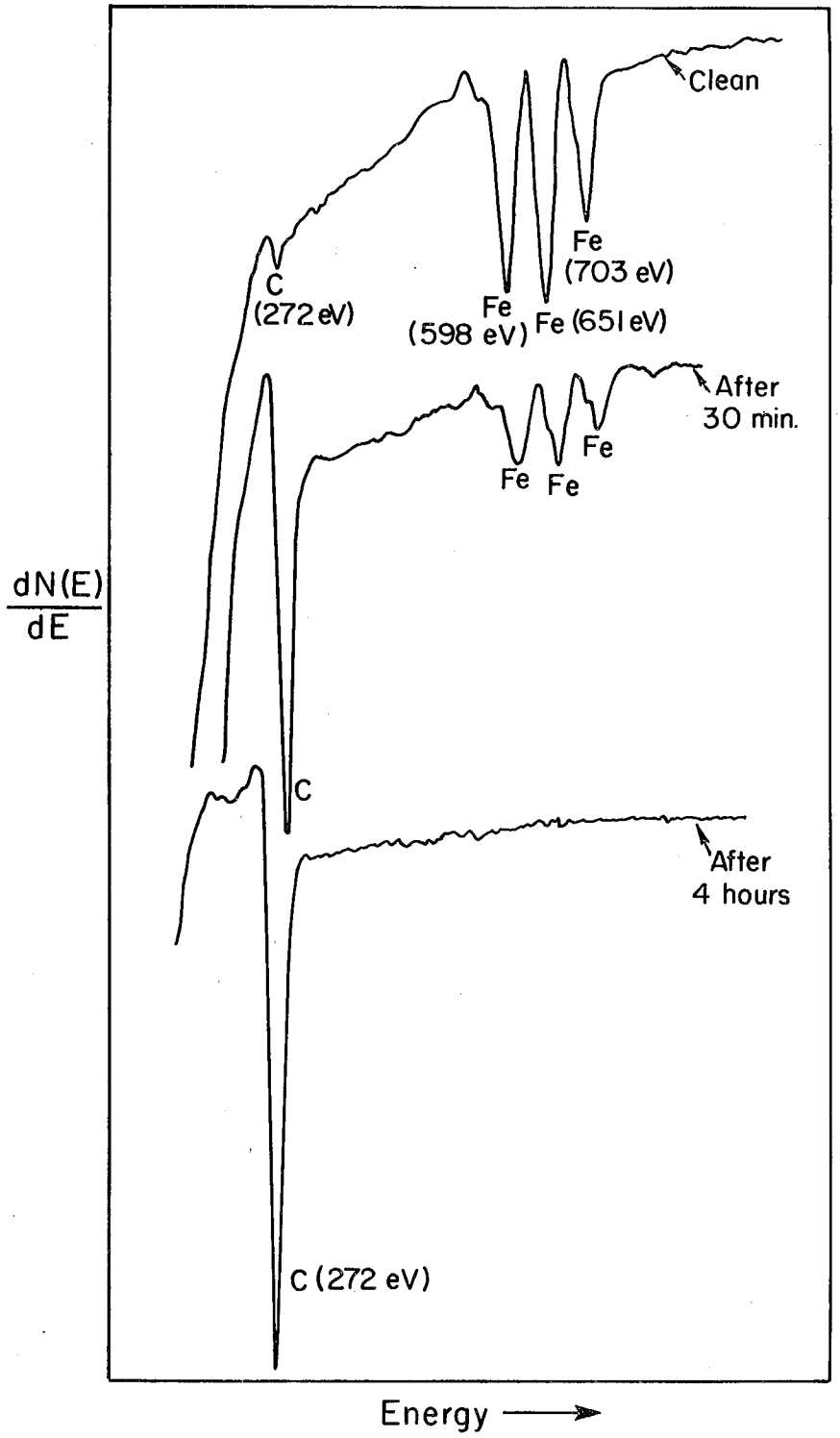

100
90
80
70
60
50
40
30
20
10
0
PRODUCT (mole %)
Rh
Fe
6 atm, 300°C
3:1 H2:CO
C1 C2 C3
C1 C2 C3 C4 C5
XBL 773-5208

Fig 10

0 0 0 0 4 9 0 3 5 8 2



XBL 779-6021

Fig 11

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0 0 0 0 4 5 0 2 2 9 4