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April 1984

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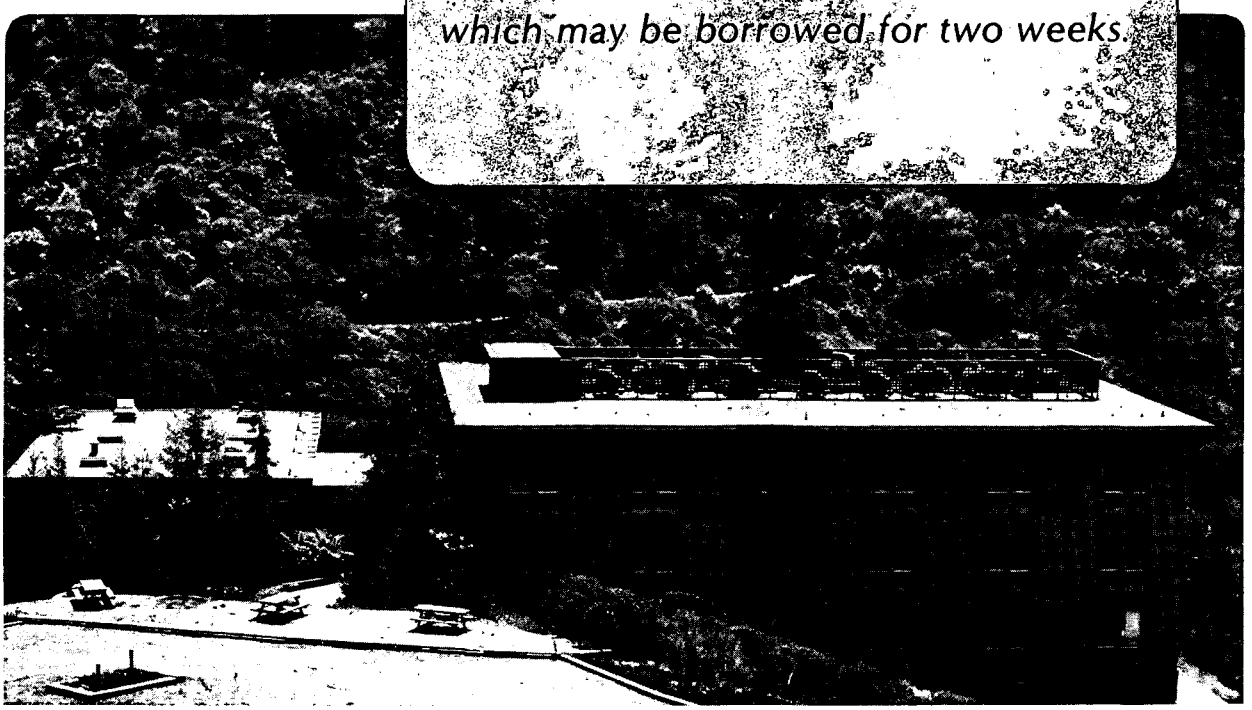

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-17965

The Hydrogenation of Carbon Monoxide Over Model Rhenium Catalysts: Additive Effects and a Comparison with Iron.

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Abstract

Small area (approximately 1 square cm) rhenium and iron foil catalysts have been studied for CO hydrogenation reactions. Rhenium produces primarily methane and showed lower activity than iron. The addition of submonolayer amounts of alkali decreased the overall rate of reaction and caused a selectivity change towards longer chain hydrocarbons on both metal surfaces. Oxidation of the surface usually caused a higher selectivity towards methane, and a decreased rate of carbon build-up, but the overall rate of methanation remained relatively constant. The hydrogenation of carbon or CH_x fragments appears to be the rate determining step in the reaction.

Introduction

The hydrogenation of carbon monoxide to produce hydrocarbons at a high rate and selectivity is under intensive study in many laboratories. Many different transition metals and transition metal compounds have been identified as good catalysts to produce C_1 hydrocarbons (methane,methanol),[1] high molecular weight liquid fuels[2] or oxygenated molecules (acetaldehyde and higher alcohols).[3] Often promotion by potassium yields increased molecular weight products and a lower concentration of methane,[4] while transition metal oxide catalysts produced more of the oxygenated species.[3,5,6]

Rhenium has received relatively little attention as a catalyst in comparison with other transition metals. Nevertheless, rhenium has recently been shown to be a very active catalyst for ammonia synthesis.[8] CO and N_2 bond scission are thought to be prerequisites for both ammonia synthesis (N_2/H_2) and CO hydrogenation (CO/H_2). Since iron is known to be active in both reactions and rhenium is active for the ammonia synthesis, it can be inferred that rhenium might also display good catalytic behavior for CO hydrogenation. In one survey study, promoted rhenium oxides on silica support were reported to have high selectivity for alcohol production.[7]

The purpose of this report is to explore the catalytic activity of rhenium metal foil for the hydrogenation of CO when clean and in the presence of potassium and oxygen and to compare its activity and selectivity with that of iron.

Experimental

All work was performed in a combined ultrahigh vacuum - high pressure catalysis chamber shown schematically in Figure 1. In its UHV mode, the chamber was equipped with a double pass CMA for Auger electron spectroscopy (AES), a UTI mass spectrometer for thermal desorption spectroscopy (TDS), an alkali deposition gun, an argon ion gun, and a molecular doser. While still positioned in the main chamber, the sample could be enclosed in a special high pressure cell to allow reactions to be performed at pressures as high as 10-20 atmospheres. The iron foil was initally cleaned by first baking it in 1 atmosphere of hydrogen (to help remove bulk S and C), then by repeated sputtering in 10^{-5} torr Argon while heat cycling between 400 and 800 C. The rhenium sample was cleaned by heating the sample to 1000 C in 5 x 10^{-7} torr oxygen for several minutes, followed by argon ion sputtering at 900 C with intermittent annealing to 1300 C. Both the rhenium and iron samples were given a final 5 minute argon sputtering at room temperature followed by flashing to 1300 and 650 C respectively. This final heating was necessary to produce an atomically smooth surface - several reactions were run on surfaces which had not been annealed, and initial methanation rates were found to be as much as an order of magnitude greater than those from the flat surface. Potassium and sodium were deposited in vacuum from a "SAES getters" potassium gun[9] mounted 3 cm from the sample. Oxygen was introduced at ca. 5 x 10^{-7} torr to oxidize both the samples and the alkali adlayers. The alkalis were readily oxidized at ambient temperature, while the clean rhenium and iron samples were heated at 800-900 and 400-500 C respectively to enhance the rate of low pressure oxidation. Oxidation could also be achieved by introducing water into the reaction cell before or during the reaction.

Once the surface was prepared, the catalytic reaction chamber was closed and a mixture of CO and H_2 gases was introduced. The $CO:H_2$ ratio was 1:4 with a total pressure of 2 atmospheres,except as noted. From room temperature, the sample was rapidly heated resistively to a given temperature (as monitored by a Pt/PtRh thermocouple wire) and gas samples were periodically introduced into the gas chromatograph by a sampling valve. Our chromatograph permitted the monitoring hydrocarbons up to C_6. Following a run, which usually lasted from 1-5 hours, the reaction chamber was evacuated to 10^{-4} torr. Then the sample was exposed to UHV, and AES and TDS were used to examine the surface.

Results

Figure 2 shows an example of the results of methane accumulation versus time for a rhenium iron foil. The runs were characterized by a by a long stable period of constant reaction rate, which would eventually decay after several hours. As will be discussed below, this decline in the rate of methane formation is attributable to the slow build-up of a carbonaceous layer which poisoned the surface.

From the rate of methane production at various temperatures, Arrhenius plots were constructed. Figures 3 and 4 show Arrhenius plots for various runs on rhenium and iron foils. The slope of the plots allowed determination of the activation energies of the reactions, and the temperatures at which rapid surface poisoning began - where the linear plot started bending over.[10] Methane was the dominant product on most initially clean rhenium samples that were studied.

The activation energies and the selectivities of rhenium and iron foils are displayed in Figure 5. The turnover frequencies (molecules/site/sec) reported were the maximum values reached by the catalyst following an induction period (usually less than 20 minutes after initiation of the reaction). The turnover frequency listed assumed an active number of surface sites of 10^{15}.

Figure 6 shows how the selectivities changed as a function of temperature. As noted in Figure 5, the activation energy for ethylene formation was lower than that for methane. Thus methane production should be favored by higher temperatures, as was observed.

The poisoning of rhenium and iron appears to be caused by carbon build-up. Figure 7 shows a close-up of the carbon AES peak after two different reactions. The amount of carbon on the surface after a given run was a function of catalyst pretreatment, reaction temperature, and reaction time.

Figures 8 and 9 show the product distributions over the rhenium and iron surfaces following alkali and oxygen promotion. The general pattern observed with alkali promoters was a change in selectivity towards higher molecular weight products as well as a decrease in the rate of methanation. The effect was more marked with rhenium than with iron, as clean iron already produces a large fraction of higher molecular weight species.

Preoxidation of the surface caused an opposite effect to what was observed with the addition of potassium, a higher selectivity towards methane. A problem occurred here concerning the number of active sites to be used in calculating turnover frequencies (in Fig. 3). Oxidation tends to increase the surface area of the catalyst. In addition, the degree of oxidation changes throughout the

reaction as a function of catalyst temperature, reaction time, and partial pressures. We believe however that our values are correct to within 50%, as our results are in good agreement with the behavior of industrial iron Fischer-Tropsch catalysts.[5]

Discussion

Rhenium metal appears to be a methanation catalyst that produces CH_4 at lower rates than either nickel or iron but with an activation energy that is similar to these two more active metals. Thus, the mechanism for producing methane is likely to be similar, i.e. CO dissociation followed by sequential hydrogenation of the carbon and the CH_x fragments. The large carbon build-up on the rhenium surface indicates that CO dissociation is facile and also that the hydrogenation step is likely to be rate determining. In this circumstance,a deuterium isotope effect is expected and experiments are in progress to ascertain its presence.

The degree of carbon build-up on the samples was measured by AES. It was thus possible to distinguish between an active "carbidic" carbon, and an inactive "graphitic" one (see Figure 7). This classification has been discussed extensively by other authors[10] and results from a comparison of the post reaction carbon AES peak shape with known peak shapes of metal-carbide and graphite surfaces. The overlayers also contained large amounts of adsorbed (or trapped) oxygen, hydrogen and hydrocarbons, as was noticed in thermal desorption following the reaction. Therefore, the carbidic overlayer should not be considered as simply a metal carbide, but a complex overlayer consisting of species where metal-carbon, carbon-hydrogen, and

carbon-oxygen bonds exist. "Carbidic" carbon was the dominant surface species observed following low temperature, short reaction time experiments. "Graphitic" carbon was dominant following high temperature experiments,or after flashing any post-reaction surface to > 700K. At this temperature, carbon-carbon bonding in graphitic layers covers much of the surface.

In general, the presence of alkalis on the surface accelerated the rate of carbon build-up. A commonly invoked model states that by lowering the dipole field at the surface, potassium allows the metal to more easily backdonate into the CO 2π antibonding orbitals [9,11,12] which then can readily dissociate at reaction temperatures. This results in increased atomic carbon on the surface and hence an increase in the carbon to hydrogen ratio. Consequently, the decreased overall reaction rates in the presence of the potassium can be explained by the change in carbon to hydrogen ratio, assuming that hydrogenation is the slow step.[10] If CO dissociation were the rate determining step, the presence of the alkali would likely result in an increased reaction rate.

The altered surface carbon to hydrogen ratio can also explain the change in selectivity towards high molecular weight species. This should occur since the rate of carbon-carbon bond formation will be increased relative to the rate of carbon-hydrogen bond formation. Potassium also caused a slight change in selectivity from alkanes to olefins in our study. This effect is even more marked on actual industrial catalysts.[4,13,14] Potassium has been shown to lower the olefin desorption barrier in a separate study.[15] It is therefore reasonable to correlate the potassium caused lowering of the desorption barrier with the relative increase in olefin production.

In recent studies by Dwyer and Hardenbergh on iron foils and powders (19,20) it was shown that the poisoning of iron foils by carbon deposition was not observed for iron powders. Although the turnover frequencies on powders were lower than those observed on foils, they showed that even the bulk iron carbide (Fe_5C_2) powder created during a reaction displayed behavior on both unpromoted and alkali promoted samples which was similar to known industrial reactivity (and that described in this work). In addition, they showed that the carbonaceous layers on iron powders contained more and longer hydrocarbon chains when alkali was used as a promoter.

The effect of pre-oxidation of the rhenium and iron surfaces depended upon several parameters including the following: 1) the degree to which the surface was pre-oxidized, 2) the temperature and time of the reaction, and 3) the presence of potassium on the surface. The extent of catalyst oxidation grew when water was introduced into the gas-phase, allowing the surface to better resist the carbon build-up so apparent in most of the experiments. Although the initial reaction rates did not increase, the rate of poisoning was slower for oxidized surfaces.

Another significant change induced by oxidation was the change in selectivity towards lower molecular weight species. By reducing both the amount of surface carbon and the number of adjacent metal atoms, the oxide surface does not permit extensive C-C bond formation. No significant amounts of oxygenates were detected over our low surface area rhenium and iron foils, in contrast to high surface area promoted industrial catalysts.[4,5,7]

This study signals the beginning of our exploration of rhenium catalytic

chemistry. As the synthesis of ammonia as well as CO dissociation and hydrogenation can take place on the metal surface we hope to explore the combined reaction involving NH_3 H_2 and CO to produce nitrogen containing organic molecules. We are currently exploring the catalytic chemistry of higher oxidation state rhenium compounds,rhenium oxides,sulfides and oxycarbides.

Conclusion

Rhenium metal has been shown to be less active than iron and to have a relatively low selectivity towards higher molecular weight hydrocarbons. Thus rhenium acts more like nickel than iron in its CO hydrogenation behavior. Alkali monolayers decreased the reaction rates and changed the selectivity towards higher molecular weight species. These effects result from a higher carbon to hydrogen ratio on the surface. Our results are consistent with both the known industrial behavior[4,5,6] and recent UHV experiments showing an increased tendency for CO to dissociate when alkali is coadsorbed.[16,17,18] The oxidation of the surface caused selectivity changes to lower molecular weight products.

Acknowledgement

This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098, and Union Carbide under grant subcontract #04927.

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Figure 1 High Pressure - Low Pressure chamber for catalytic surface studies.

Figure 2 Product accumulation curve for CO hydrogenation over oxidized iron foil. $H_2/CO = 4/1$; 1 atm.

Figure 3 Arrhenius plot of methanation reaction on iron. $CO/H_2=1/4$, 32 psi.

Figure 4 Arrhenius plot of methanation reaction on rhenium. $CO/H_2 = 1/4$, 32 psi.

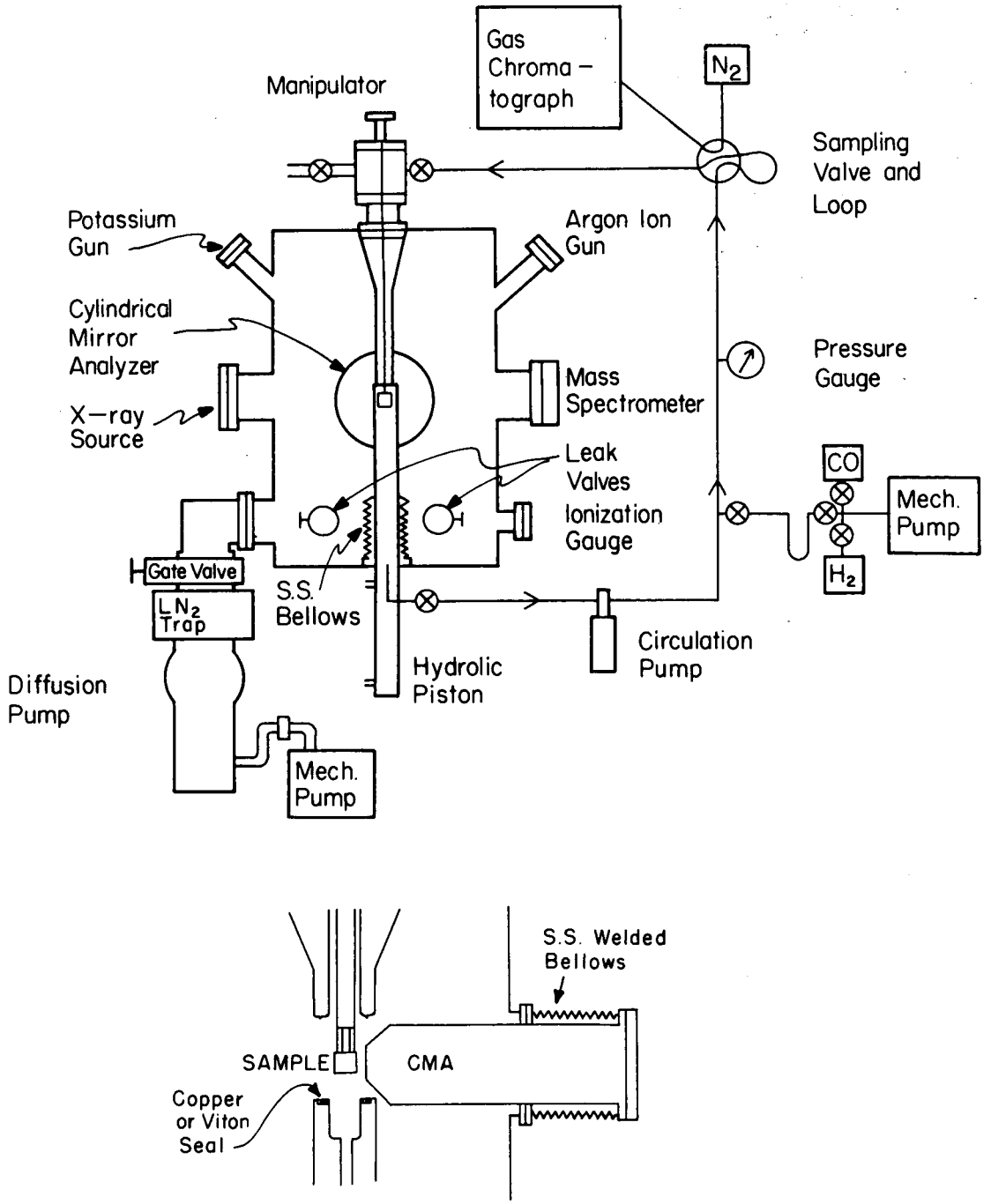
Figure 5 A comparison of the selectivities for C_1 and C_2 species at 540K, $CO/H_2 = 1/4$, 32 psi, over iron and rhenium foils.

Figure 6 Product selectivity and temperature dependence for CO hydrogenation on rhenium foil, $CO/H_2 =1/4$, 32 psi.

Figure 7 Auger spectra for graphitic and carbidic overlayers on iron foil.

Figure 8 The effect of oxidation on product selectivity

Figure 9 The effect of alkali addition on product selectivity.



SIDE VIEW WITH HIGH PRESSURE CELL OPEN

XBL 832-8401

Fig. 1

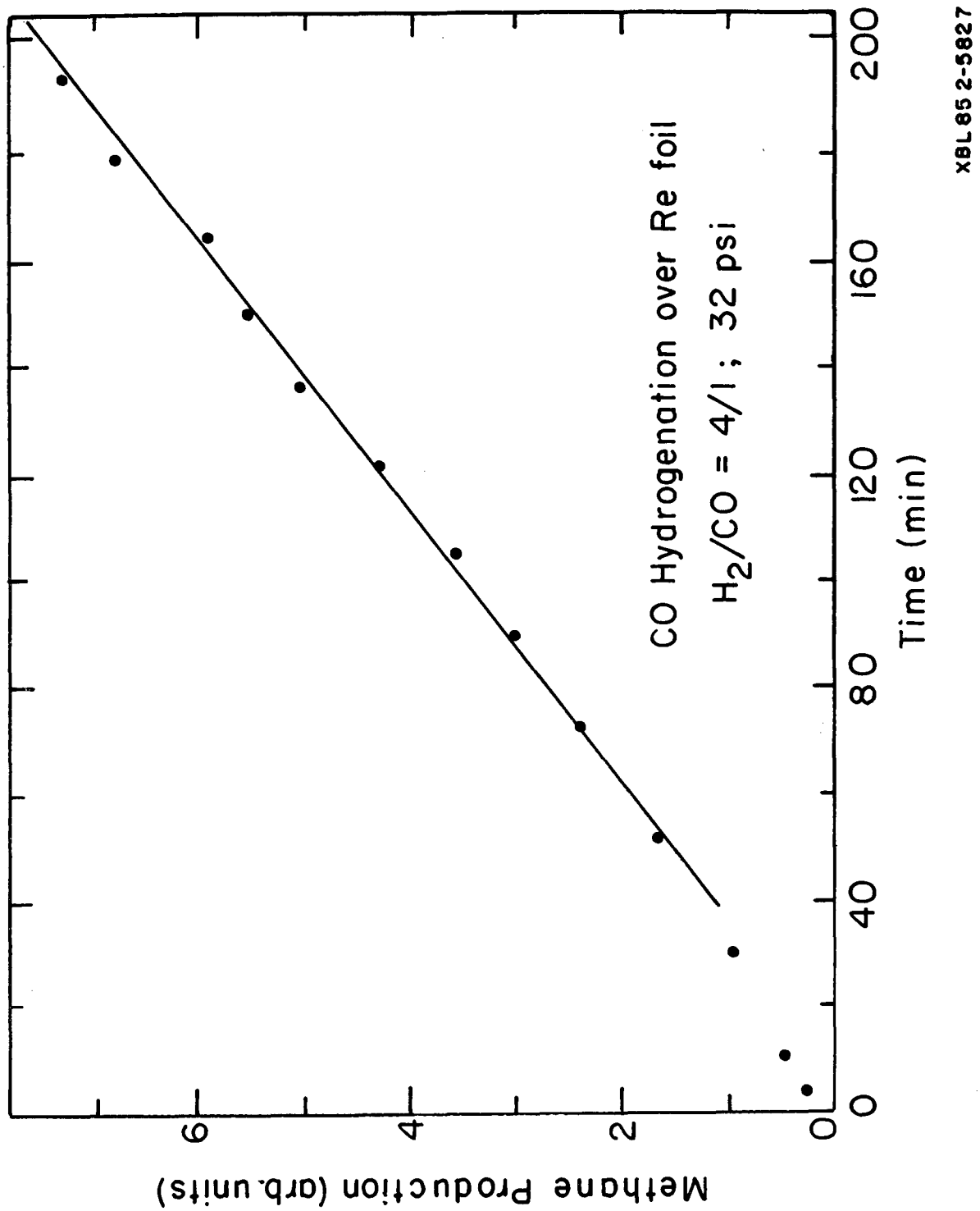

CO Hydrogenation over Re foil
$H_2/CO = 4/1$; 32 psi
Methane Production (arb. units)
Time (min)
0
2
4
6
0
40
80
120
160
200
XBL 852-5827

Fig. 2

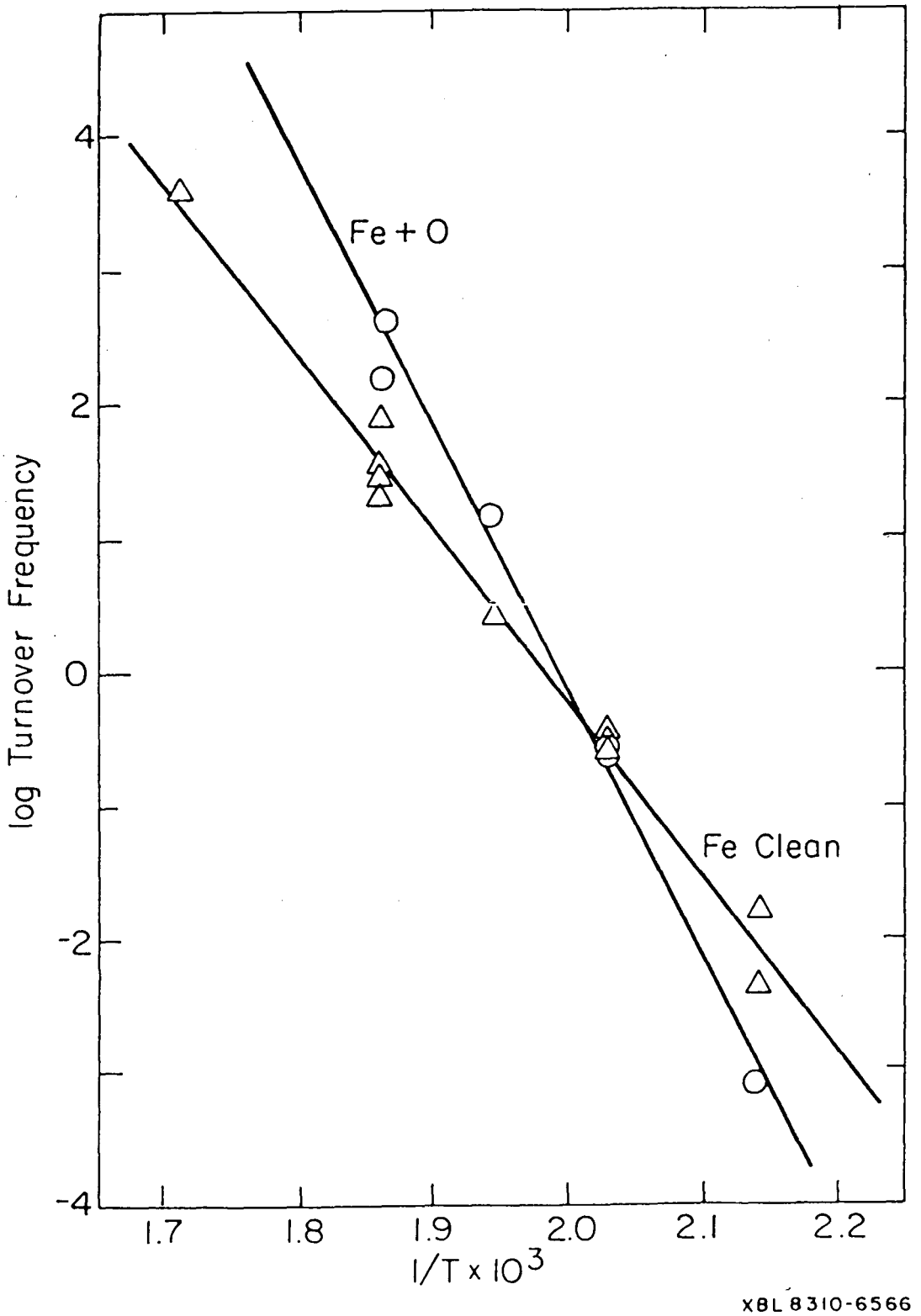

Fe + O
Fe Clean
log Turnover Frequency
4
2
0
-2
-4
1.7
1.8
1.9
2.0
2.1
2.2
1/T x 10^3
XBL 8310-6566

Fig. 3

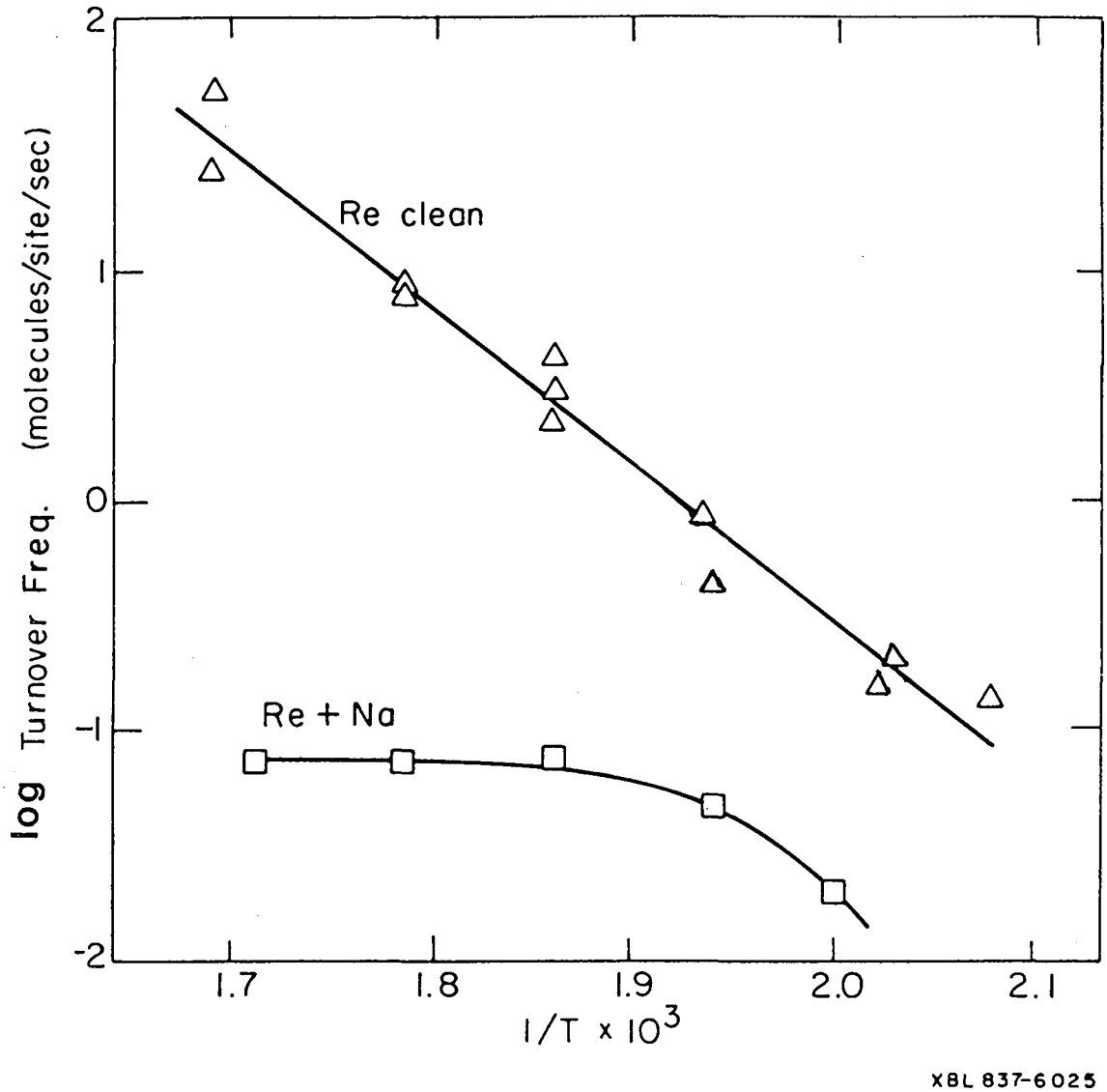
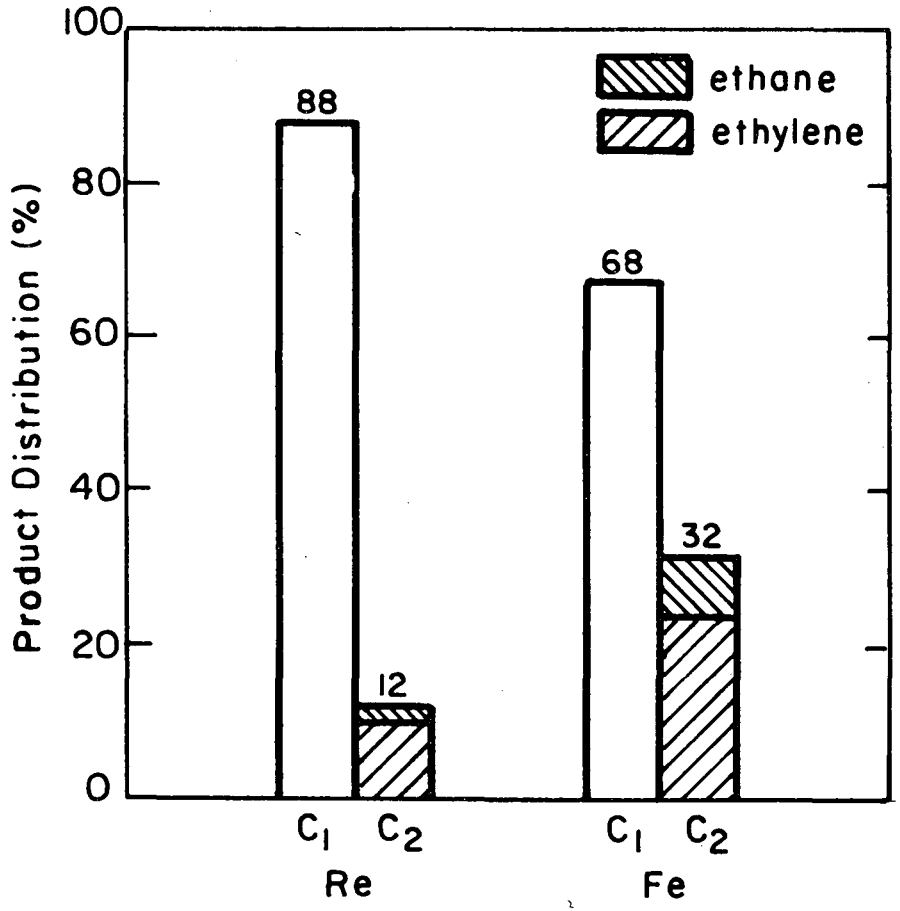

2
1
0
-1
-2
log Turnover Freq. (molecules/site/sec)
Re clean
Re + Na
1.7
1.8
1.9
2.0
2.1
1/T x 10^3
XBL 837-6025

Fig. 4



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

Fig. 5

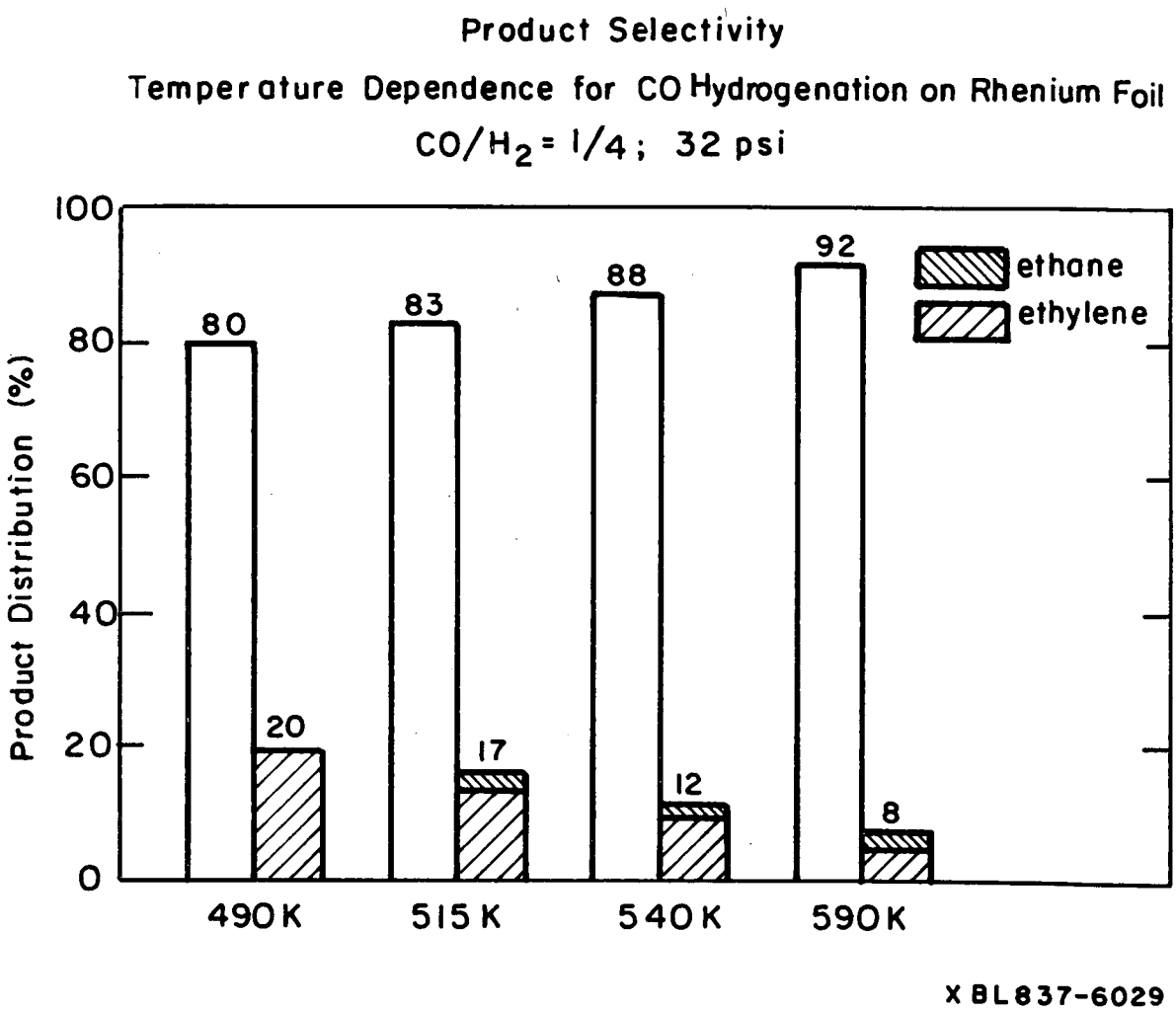

Product Selectivity
Temperature Dependence for CO Hydrogenation on Rhenium Foil
CO/H2 = 1/4 ; 32 psi
Product Distribution (%)
100
80
60
40
20
0
80
20
83
17
88
12
92
8
ethane
ethylene
490K
515K
540K
590K
XBL837-6029

Fig. 6

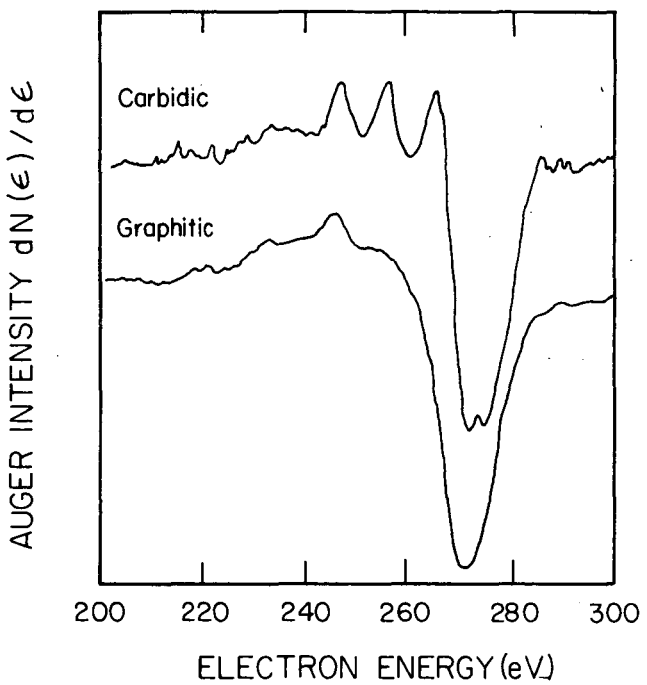


Fig. 7

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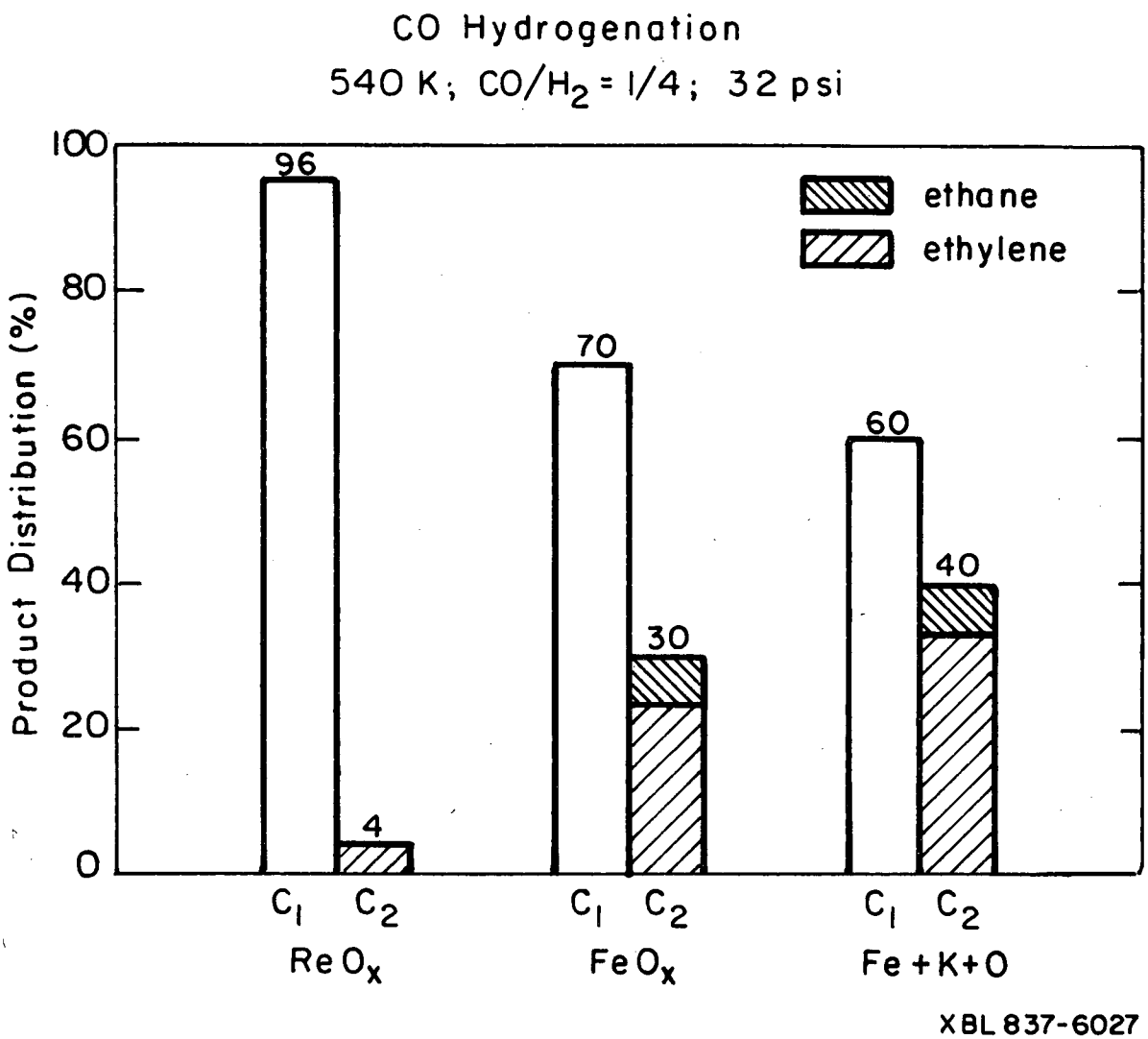

CO Hydrogenation
540 K; CO/H2 = 1/4; 32 psi
Product Distribution (%)
100
80
60
40
20
0
96
4
70
30
60
40
ethane
ethylene
C1
C2
ReOx
FeOx
Fe+K+O
XBL 837-6027

Fig. 8

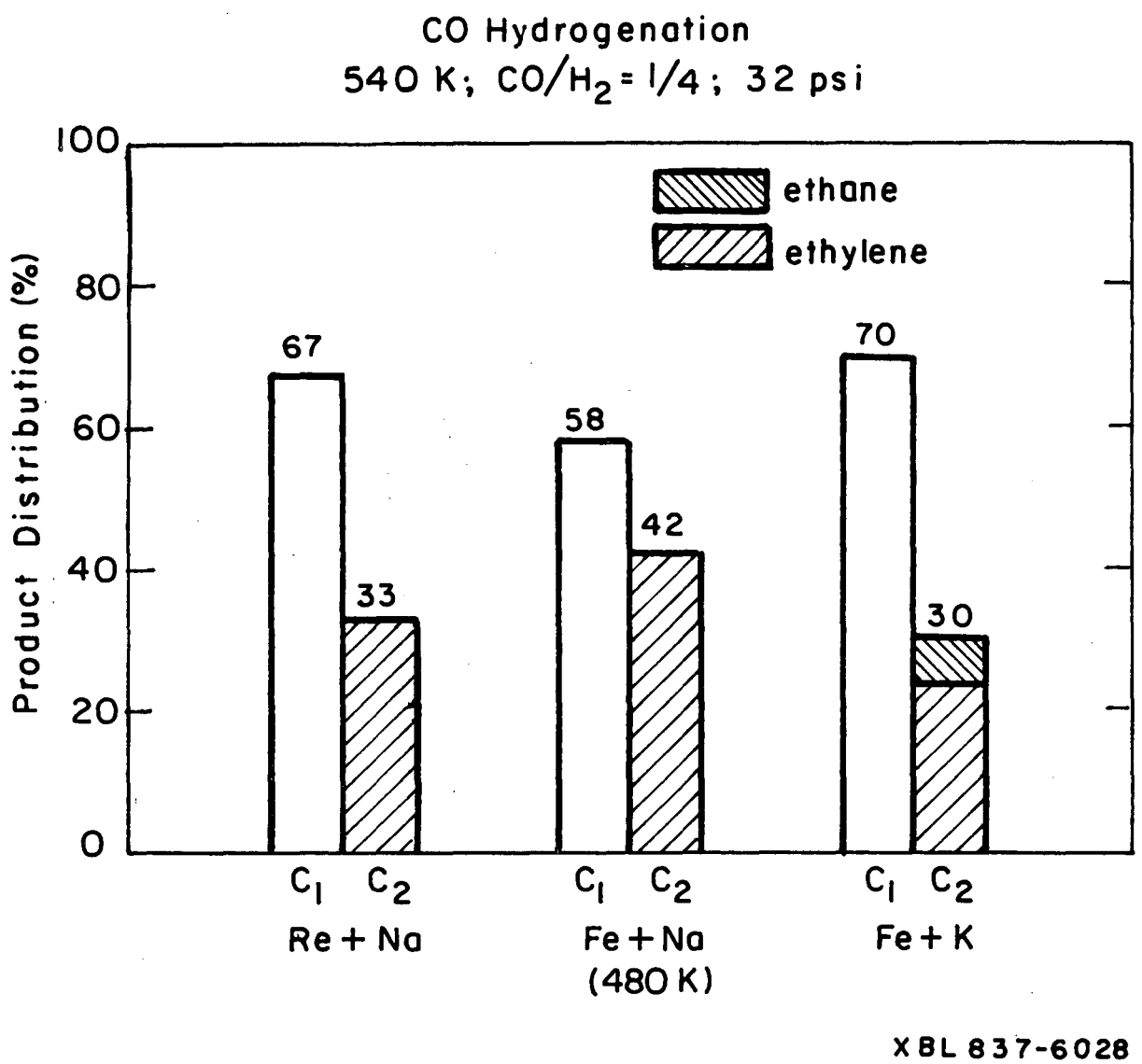
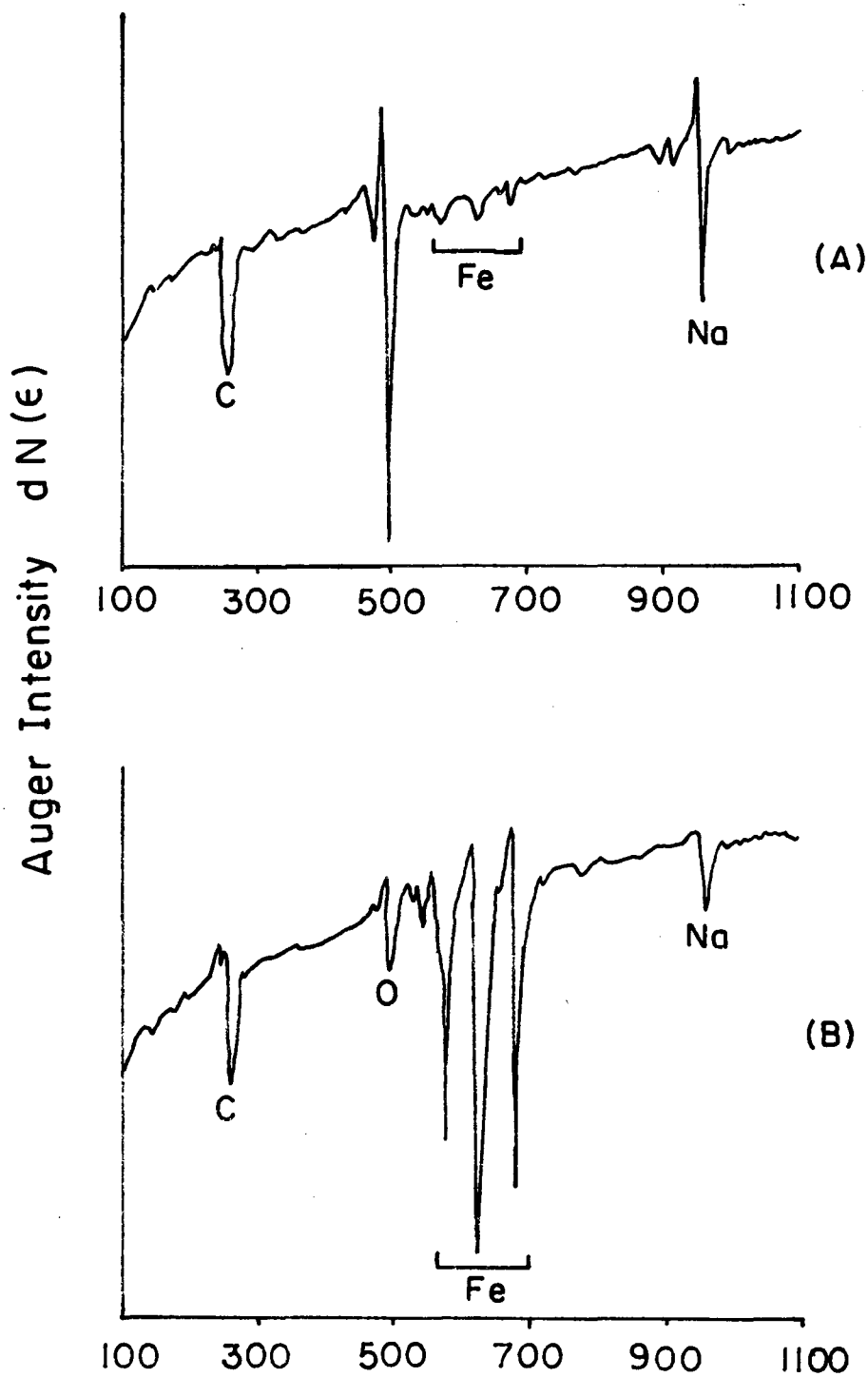

CO Hydrogenation
540 K; CO/H2 = 1/4; 32 psi
Product Distribution (%)
100
80
60
40
20
0
ethane
ethylene
67
33
58
42
70
30
C1 C2
Re + Na
C1 C2
Fe + Na
(480 K)
C1 C2
Fe + K
XBL 837-6028

Fig. 9



XBL 838-11132

Fig. 10

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