

Further Results on the Reaction of H_2/CO on Fused Iron
by the Transient Method

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Introduction

In a previous study (1) it has been proposed that the surface of a promoted fused iron catalyst is largely covered with carbon during the steady-state reaction of hydrogen and carbon monoxide (90% H_2 , 10% CO) at atmospheric pressure and 250°C. This same catalyst, a commercial ammonia synthesis catalyst (CCI), was also evaluated (at 2.0 MPa) in a more applied way in connection with the study of a scheme for energy storage in a central power plant (2, 3). It is now clear that it is necessary to consider that each catalyst (i.e., even the same metal on different supports) may operate for reactions of H_2/CO through a unique sequence of steps, or at least with a particular rate-determining step. Thus although the hydrogenation of surface carbon seems to be rate-limiting on iron (1), on ruthenium the dissociation of adsorbed CO has been proposed as rate limiting (4). The present work is a continuation of that of reference (1); this time the role of CO_2 and H_2O has been investigated, and interesting information has been obtained on the chain growth process.

Experimental

The reactor was made of 1/4-inch stainless steel tube and filled with 100 mg of catalyst (particles of 300 μm) mixed with 500 mg of glass beads of the same size. The reactor and the glass beads were confirmed to produce no products at the reaction conditions. Feed rates of H_2/CO (9/1) between 20 and 120 ml/min were explored but if not otherwise noted, 40 ml/min was used; the conversion was always less than 5% of the CO fed.

Hydrogen (99.99%, Air Liquide) was purified by a molecular sieve (5A) trap, followed by a deoxo reactor, followed by a second molecular sieve 5A. Carbon monoxide (99.9%, Air Liquide) was passed through a glass tube heated to 220°C to decompose carbonyls and then through a trap of activated carbon at 25°C.

Analysis of the reaction products was by gas chromatography. For the separation of the hydrocarbons, a Poropak Q (80-100 mesh) 6-m, 1/8-inch stainless steel column was used with a flame ionization detector. Column temperature was 195°C, and the carrier gas (He) was used at 30 ml/min. The CO_2 and H_2O were measured by a second identical Poropak Q column at 175°C, leading to a thermal conductivity detector. For the reaction conditions used, only alkanes were found among the hydrocarbon products.

Results

The Basic Reaction

After an initial reduction in flowing hydrogen at 60 ml/min for 60 hours at 500°C, the reactor is cooled to 250°C, and the feed is switched at time zero to 10% CO in H_2 . The curve 1 of Fig. 1 results. The deactivation is rapid and the production rate of methane passes through a maximum. A reactivation in H_2 at 500°C

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for 15 hours increases the activity of the catalyst to a level above what it was at the end of the first run, but below what it was at its maximum. This process continues with further reactivations, and Fig. 1 shows curves after 10 reactivations and after 20 reactivations. However, it was found that a short (30 min) treatment by oxygen at 500°C and 1 atm before the usual reduction by hydrogen produced a relatively stable catalyst, as shown by the curve O₂ of Fig. 1. The activity of the catalyst is obviously very sensitive to its state of oxidation and to the concentration of refractory carbon at or near its surface. It may be recalled that Matsumoto and Bennett (1) found that short treatments in helium at 250°C converted the active carbon intermediate to a form inactive at this temperature. Similar effects are observed for nickel (5).

Figure 2 shows the other hydrocarbons produced corresponding to the curve labelled O₂ on Fig. 1. The numbers by the curves are the steady-state rates of production divided by that for methane. These selectivities are insensitive to the activity level and are about the same for all the catalyst conditions of Fig. 1. Water and carbon dioxide are also produced, but these production rates are less reproducible. The catalyst has a fraction exposed of only about 5 percent, and it has been shown that the entire mass of iron is carburized (1). Thus small changes in carbon concentration in the bulk may produce CO₂ and H₂O at rates at least as high as the catalytic reaction. Figure 3 shows the history of a freshly reduced catalyst after exposure to CO/H₂ at 250°C, H₂ at 250°C, and finally H₂ programmed to 500°C. The first peak represents the removal of a surface carbon intermediate as methane, and the second large peak comes from the decarburization of the bulk of the catalyst. This result has already been discussed (1).

Another aspect of the reacting system can be seen in Fig. 4. Experiments were started with a feed rate of 120 ml/min, but the conversion (0.003 to CH₄) was not sufficient to obtain reliable analyses for H₂O and CO₂ by chromatography (thermal conductivity detector). The hydrocarbons, however, were analyzed correctly (flame ionization detector). When the conversion was increased (0.006 to CH₄) by reducing the feed rate to 20 ml/min, a much lower formation rate of methane was observed. This reduction in activity can only be explained by inhibition of the rates by products of the reaction; the reactant concentrations are of course almost unchanged. In other words, even at these low conversions the reactor is not truly differential.

We are thus led to investigate the effect of the products of reaction on the reaction rates, and these experiments will be described later. In order not to be misled by secular changes in the catalyst, a steady state condition is first established with 10% CO + H₂ feed. The feed is then changed to one containing H₂O, CO₂, etc. as desired, and finally it is changed back to 10% CO + H₂.

The base reaction has been studied at several temperatures (230°, 250°, 270°, and 300°C), and an activation energy of 20.4 kcal/mole is observed, similar to the value found at 2.0 MPa (2).

Influence of CO₂

To the reaction mixture 10% CO + H₂ was added 5% CO₂. The CH₄ production diminished by about 8%, and when the CO₂ was removed the methane formation rate regained its initial value. This effect is not sufficient to explain Fig. 4.

If the CO in the feed gas is replaced by CO₂, the methanation reaction continues at a lower rate, as shown in Table 1. The formation of higher hydrocarbons, however, is drastically reduced. The CO₂ is dissociatively adsorbed, but the surface oxygen concentration is increased.

Influence of Water

A concentration of 0.6% water vapor was added to the 10% CO + H₂ feed mixture at steady-state reaction, and Fig. 5 shows the result. The inhibiting effect of water is clear, and it is probable that the lower rates at higher conversion shown in Fig. 4 are explained by the increased water concentration at higher conversion.

It is also interesting to evaluate the capability of the steady-state catalyst surface to catalyze the shift reaction. Figure 6 indicates that when the H₂ in the 10% CO + H₂ mixture is replaced by 0.6% water, all production of hydrocarbons stops, and a large rate of CO₂ formation is observed. These results are further evidence of the power of the iron catalyst to adsorb dissociatively H₂ as well as CO.

Influence of Ethane

The addition of 10% C₂H₆ to the reactants does not change the rates of reaction. However, iron has some activity for hydrogenolysis (6). If the 10% CO + H₂ mixture is changed to 10% C₂H₆ + H₂, methane is formed at 0.65 μ mole/g min (see Fig. 7), less than 10% of a typical methanation rate.

Influence of Olefins

When 10% C₂H₄ + H₂ is fed to the reactor just after the reduction of the catalyst at 500°C, the curves of Fig. 7 are obtained. There is immediate production of methane, propane, n-butane, and n-pentane. Ethane is confounded with the large ethylene peak in the analysis by chromatography. The rates do not increase from zero as in Fig. 2. A switch to hydrogen (not shown on Fig. 7) produces no methane peak at 250°C, and programming the temperature to 500°C results in the production of only 4 μ moles of CH₄/g of iron. Thus the C₂H₄/H₂ mixture does not carburize the iron at 250°C. The reaction rates after 4 hours with ethylene are about twice those with CO, and the initial rates are an order of magnitude higher. Figure 7 shows also the switch from C₂H₄/H₂ to CO/H₂ and then to C₂H₆/H₂.

Figure 8 shows the usual curves for CO/H₂ over a reduced catalyst, followed by a switch to C₂H₄/H₂ over the now carburized catalyst. These results are consistent with the idea that the rate-determining step with CO is the hydrogenation of surface carbon. Subsequent chain growth occurs through CH₂ groups (or CH), and if these groups are formed directly from ethylene, the production rates of the products are higher; the rate limiting step coming from CO is no longer relevant. The C₂H₄/H₂ reaction occurs on iron, and after exposure of the catalyst to CO/H₂, much of the surface is covered with carbon, so the rate of CH₄ production with C₂H₄/H₂ of Fig. 8 is lower than that of Fig. 7.

Figure 9 shows the reaction of 10% C₃H₆ + H₂ over the reduced catalyst. The results are qualitatively the same as with ethylene. Butene-2/H₂ reacts as shown in Fig. 10, and butene-1/H₂ (always 90% H₂) gives rates that are all a bit lower than for butene-2, as shown. All these results emphasize that on the iron surface the CH₂ or CH fragments come rapidly to a steady state; the rates of production of the alkane products (no olefins were observed) are not appreciably influenced by the source of the CH₂ groups on the surface. However, there are some differences, as shown in Table 2, which gives the ratios of the production rates after 4 hours. Starting from a given olefin, the products are mostly of shorter chain length, and close to the chain length of the reactant. In any event, we are justified in supposing that, starting from CO/H₂, all the steps after CH₂ or CH formation are rapid, and little of the surface is covered by chain fragments at 250°C and 100 kPa.

Discussion

The new results of the present study confirm most aspects of the sequence of steps proposed by Matsumoto and Bennett (1). CO is adsorbed as C + O, and the freshly formed surface carbon is the most abundant surface intermediate; its hydrogenation by adsorbed hydrogen present as H is the rate-determining process. Carbon dioxide added to CO/H₂ is not strongly enough adsorbed to affect the rate appreciably. However, in the absence of CO, CO₂/H₂ makes methane at a lower rate; the surface is more oxidized, and the active C is present in lower concentration than in the presence of CO.

However, water can compete with CO for the surface, and it oxidizes the surface while reducing the active C coverage by forming CO₂. The high reaction rate of CO/H₂O to CO₂ rather than CH₄ shows the strong affinity of the surface of the iron catalyst for oxygen (Figs. 5-6).

We recall that the rate of hydrocarbon production over a freshly reduced catalyst rises from an initial value of zero. The carbon formed from CO reacts with the bulk iron of the catalyst, and the surface carbon necessary for hydrocarbon production gradually increases in coverage as the bulk of the iron is carburized to Fe₂C at 250°C. However, when C₂H₄/H₂ is passed over the reduced catalyst, no active C intermediate seems to be necessary. The rate starts at a maximum value, and the iron is not carburized. Thus the observed formation of CH₄ and C₃H₈ shown in Fig. 7 arises through a CH_n fragment. No oxygen is present. Iron thus behaves differently from cobalt, for which oxygen is apparently necessary for chain growth (7, 8).

When a CO/H₂ feed is changed to C₂H₄/H₂ (Fig. 8), the rate of hydrocarbon production is higher from ethylene than from CO. Methane is an important product from C₂H₄/H₂. This result is not inconsistent with the lack of ¹⁴CH₄ formed when ¹⁴C₂H₄ is added in small quantity to CO/H₂ (9). With CO present the C₁H_n groups must originate principally from CO, so that the added ¹⁴C will be concentrated principally in C_xH_y groups of x ≥ 2.

It is clear that the reaction of ethylene takes place on the iron surface, since the rate decreases as the inert graphitic carbon builds up (Figs. 7 and 8). It was shown previously (1) that the reaction from CO also occurs on the iron part of the surface; after steady state under CO/H₂, a brief exposure to H₂ alone and then a switch back to CO/H₂ leads to a temporary increase in the rate. If the exposure to hydrogen is long enough to decarburize some of the bulk, the subsequent CO/H₂ reaction rate is lowered as recarburization lowers the concentration of the active surface carbon.

A freshly reduced catalyst is carburized by the H₂/CO mixture in about an hour (recall that carburization in CO alone is much slower (1)). During this period the hydrocarbon formation rate gradually increases as the surface carbon concentration rises, as influenced by the bulk carbon (carbide) concentration. A switch to pure H₂ gives a methane peak, meaning that hydrogen reacts as H on the surface and that the surface coverage by C is high. The rate-determining process is the formation of CH_n from the surface C; subsequent chain growth is rapid and occurs through these groups, and the product distribution is determined by the rate of propagation and termination (desorption) of chains arising from CH_n. The presence of H₂O and to some extent CO₂ in the gas phase increases surface O at the expense of C and/or H, inhibiting the reaction. However, active surface carbon is gradually converted to inert (at 250°C) graphite, and activity slowly declines as the part of the iron covered with labile C decreases. For a much regenerated catalyst, oxygen followed by hydrogen cleans off a higher fraction of inert graphite than H₂ alone.

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Table 1
Reaction of CO₂ and H₂

Formation Rate, μ mole/g min.	Feed		
	Before		After
CH ₄	7.0	4.4	7.4
C ₂ H ₆	3.2	0.52	3.5
C ₃ H ₈	1.5	0.065	1.5

Table 2
Relative Production Rates
 (4 hours on stream)

Feed Mixture	$\frac{C_2}{C_1}$	$\frac{C_3}{C_1}$	$\frac{C_4}{C_1}$	$\frac{C_5}{C_1}$
10% CO + H ₂	0.6	0.29	0.10	0.02
10% C ₂ H ₄ + H ₂		0.15	0.06	0.001
10% C ₃ H ₆ + H ₂	0.49		0.087	0.002
10% butene-1 + H ₂	0.19	0.76		0.08
10% butene-2 + H ₂	0.20	0.92		0.09

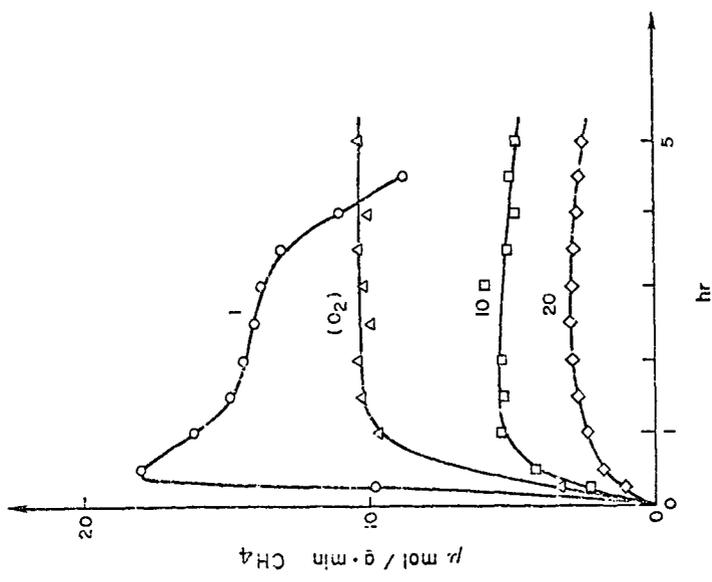


Figure 1

Rate of Reaction after Various Reactivations; Feed Rate, 120 ml/min.

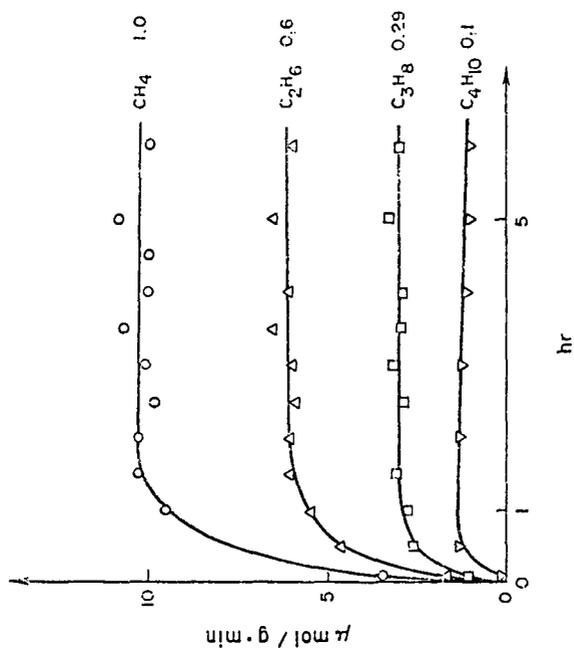


Figure 2

Formation Rates of Products.

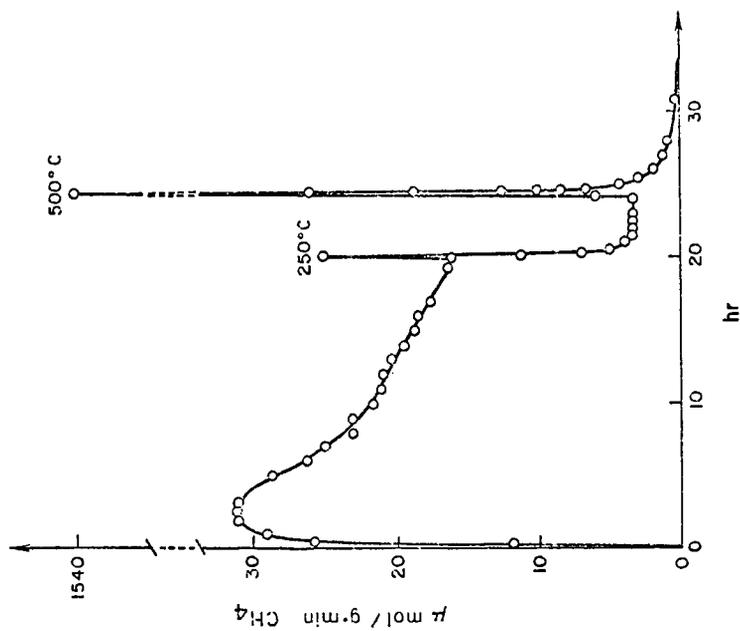


Figure 3

Hydrogenation of Surface Carbon.

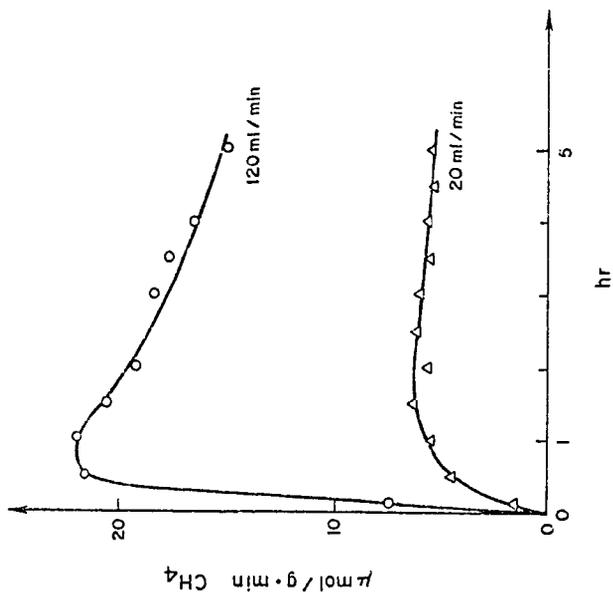


Figure 4

Effect of Flow Rate on Methane Formation.

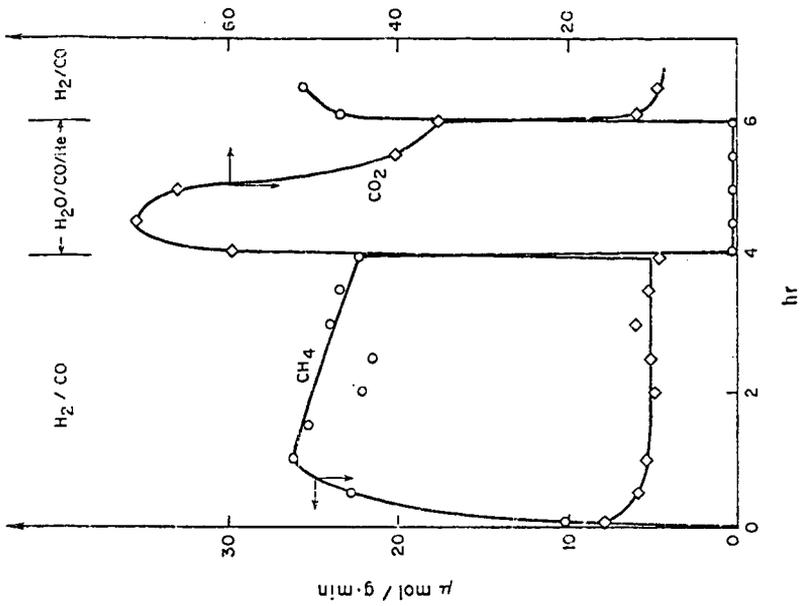


Figure 6

Reaction of Water and Carbon Monoxide.

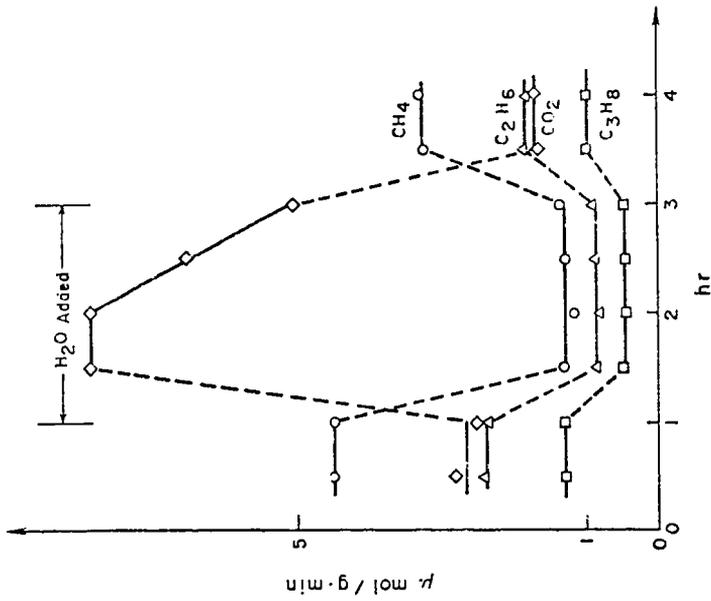


Figure 5

Effect of Water Vapor on the Reaction.

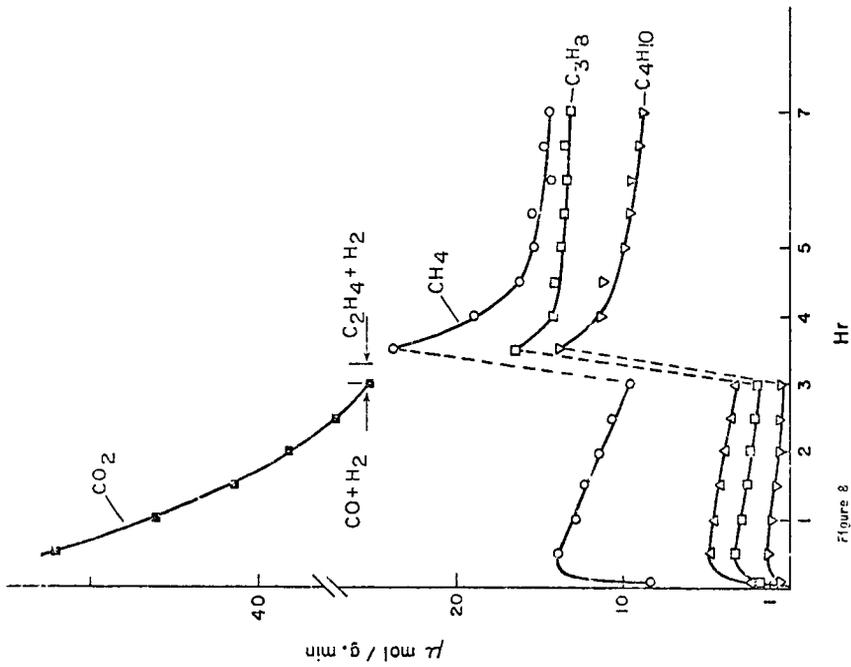


Figure 8
Reaction of Ethylene and Hydrogen
on a Carburized Catalyst.

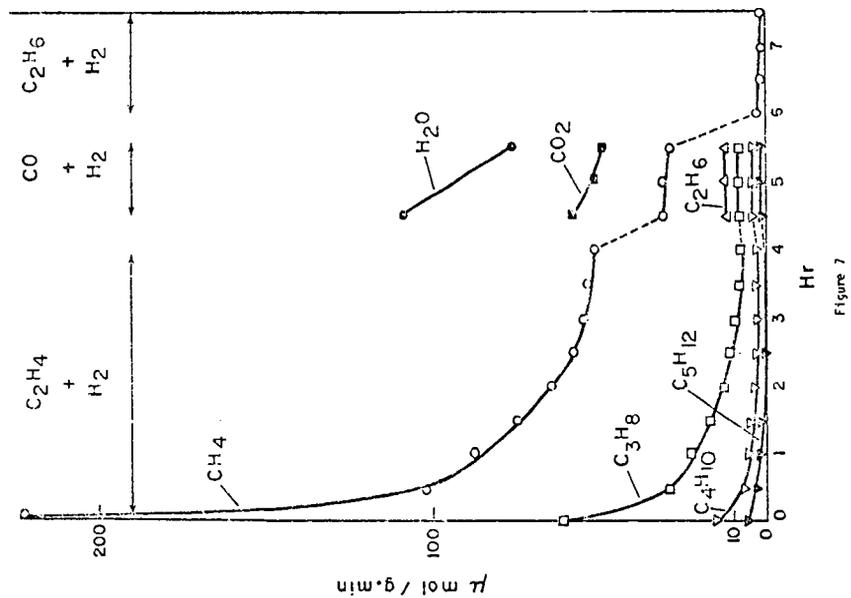


Figure 7
Reaction of Ethylene and Hydrogen
on a Reduced Catalyst.

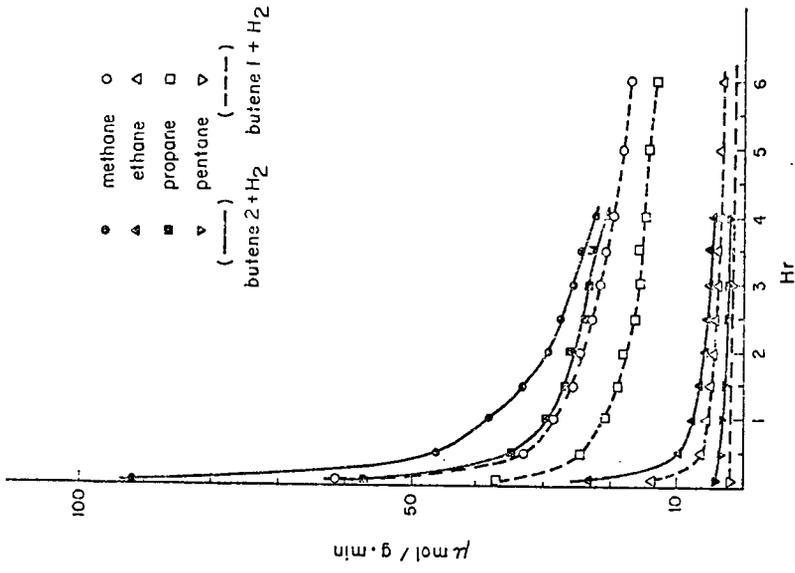


Figure 10

Reaction of Butene-1 and Butene-2 with Hydrogen.

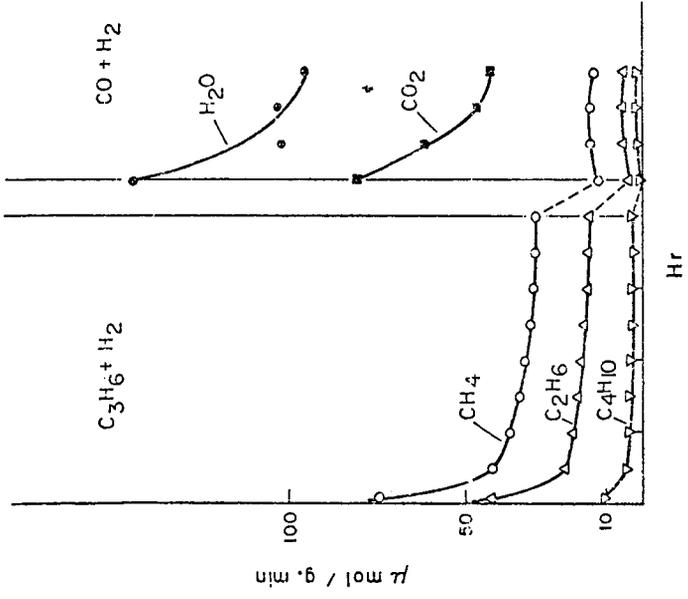


Figure 9

Reaction of Propylene and Hydrogen.