

Report 11

Fischer-Tropsch Catalyst Characterization

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NOTES ON D.O.E. PRESENTATION

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Our project has been concerned with the selective production of C_2-C_4 olefins from syn gas. Earlier catalyst evaluation work had revealed that an unsupported iron-manganese oxide catalyst gave good selectivities to C_2-C_4 with promising olefin/paraffin (O/P) ratios. Figure 1 shows product distribution for reaction of a $2H_2/CO$ mixture at 34 atm in the temperature range 210 to 300°C. The catalysts were prepared by co-impregnation and activated in H_2 at 500°C. Overall CO conversions were maintained at 7-8% by increasing temperature as Mn content increased. The C_2-C_4 fraction remained relatively constant up to about 80 mole% Mn. A significant increase in the O/P ratio of this fraction occurred with small additions of Mn to the Fe catalyst, but then declined above about 40% Mn.

One phase of this project has been devoted to a detailed examination of the catalysts in an attempt to relate catalyst properties to catalytic selectivity. Figure 2 gives the plan of study and techniques used. At this time we have completed about 2/3 of the work outlined.

Figure 3 depicts an XRD spectrum for a reduced 30% Mn-Fe catalyst. The major phases present are Fe and MnO. Figure 4 shows the presence of some FeO in the MnO phase for this catalyst (not found in all catalysts).

BET surface areas on a number of catalysts are presented in Figure 5. On both ends, the addition of the minor component increased the surface area, and a minimum is observed around 35% Mn. Chemisorption data are shown in Figure 6. CO seems to be specific for available Fe surface, whereas CO_2 increased with Mn content. Based on BET and chemisorption measurements,

proposed structures of the low and high Mn catalysts are shown in Figure 7. The drop in CO and O₂ chemisorption in conjunction with an increase in BET area for the low Mn catalyst is interpreted in terms of MnO platelets covering the basic Fe particles. For the high Mn catalyst, separate particles of Fe and MnO are proposed.

It is well known that Fe catalysts form carbides in the presence of CO/H₂. Figure 8 shows weight gain data for the iron catalyst at 250°C in a 3H₂/CO stream. Weight gain was rapid at first, then slower. Switching to H₂ resulted in a significant weight loss and line out. At 500°C in H₂, the catalyst returned to its original weight. A similar experiment at 300°C for 65 hours showed the presence of Fe₂C(Hagg) carbide. Similar experiments by Sancier et al [ACS Petrol. Div. Prepr. 23 (2), 545 (1978)] have shown the presence of a carbonaceous residue as well as iron carbide in a carbonized Fe catalyst. Comparison of carbonization rates for Fe (C-0) and a 15% Mn-Fe catalyst (C-15) are presented in Figure 9. The latter catalyst carburized slower at both temperatures. When corrected for the amount of available iron surface area, both catalysts showed about the same rate of carburization at 300°C; however, at 225°C, the mixed catalysts carburized considerably slower. The carburization data fit Elovich kinetics (weight vs. log time), showing two distinct straight-line regions.

Temperature programmed desorption (TPD) results of CO on a Mn-Fe catalyst are shown in Figure 10. A broad, low temperature desorption peak, possibly due to two adsorption sites, was observed. After reaching 500°C, the catalyst was cooled to room temperature and the gas changed to H₂. Subsequent temperature programmed reaction (TPR) of residue left from the TPD, revealed the products (analyzed by mass spectrometry) given in Figure 11. Appreciable quantities of CH₄ and H₂O were evolved at moderate to high temperature. These results are in general agreement with other workers, indicative of dissociative adsorption of CO. Figure 12 summarizes results obtained

on the Fe catalyst, and a low Mn and a high Mn mixed catalyst. The upper set refers to TPD and the middle set to subsequent TPR. Small amounts of CO_2 were observed in the TPD of the mixed catalysts, and the high Mn catalyst gave some low temperature CO and H_2O in the TPR. In the lower set, the catalyst was first carburized at 250°C , then CO adsorbed at room temperature and TPR run in H_2 . Of interest, the Fe catalyst gave no products, signifying very little adsorption of CO on the carburized catalyst; whereas the mixed catalysts yielded CO at low temperature and reaction products at high temperature. These results show some significant differences between Fe and Mn/Fe catalysts with respect to adsorption-reaction properties of CO on the carburized catalysts. The MnO catalyst was inactive in all these experiments. This suggests that MnO modifies the character of the Fe phase (possibly at boundary phases) but is not active itself in Fischer-Tropsch synthesis.

We are currently looking at catalytic reactivity functions to gain insight into selectivity differences found with these catalysts. Figure 13 shows the effect of catalyst state on hydrogenation of 1-hexene over the Fe catalyst. The freshly reduced catalyst was very active, giving complete conversion to hexane at 50°C . After carburization, activity dropped considerably (k_H is pseudo first order rate constant). Hydrogenation of hexene over the carburized catalyst in the presence of H_2/CO reduced the hydrogenation activity even more. Since we were interested in relative hydrogenation rates in the presence of CO/H_2 , the latter conditions were employed with several mixed Mn-Fe catalysts. Figure 14 displays the results obtained. The 5% Mn-Fe catalyst gave less hydrogenation per gram than the Fe catalyst, but intrinsic hydrogenation activity was about the same. On the other hand, the 74% Mn-Fe catalyst showed a considerably higher intrinsic hydrogenation, which could account for the low O/P ratio obtained in this composition range. Arrhenius plots were not linear, probably due to some hydrogenolysis observed

at 250°C. Activation energies based on the two lower temperatures were low, possibly indicating diffusion through a carbon overlayer is rate limiting.

Note that MnO is relatively unreactive for hydrogenation.

Conclusions to date are:

1. The structure of the mixed catalysts consist mainly of bulk Fe and MnO, although some FeO may be incorporated in the MnO.
2. The MnO seems to affect the adsorption properties of CO, but CO adsorption in MnO is negligible.
3. There is a lower rate of carburization in presence of MnO.
4. Hydrogenation activity is enhanced at high level of MnO.
5. Interface regions between Fe and MnO may be responsible for these effects, resulting in differences in catalyst selectivity and O/P ratios.

HYDROCARBON YIELD VS. CATALYST COMPOSITION

(after Y.S.Tsal)

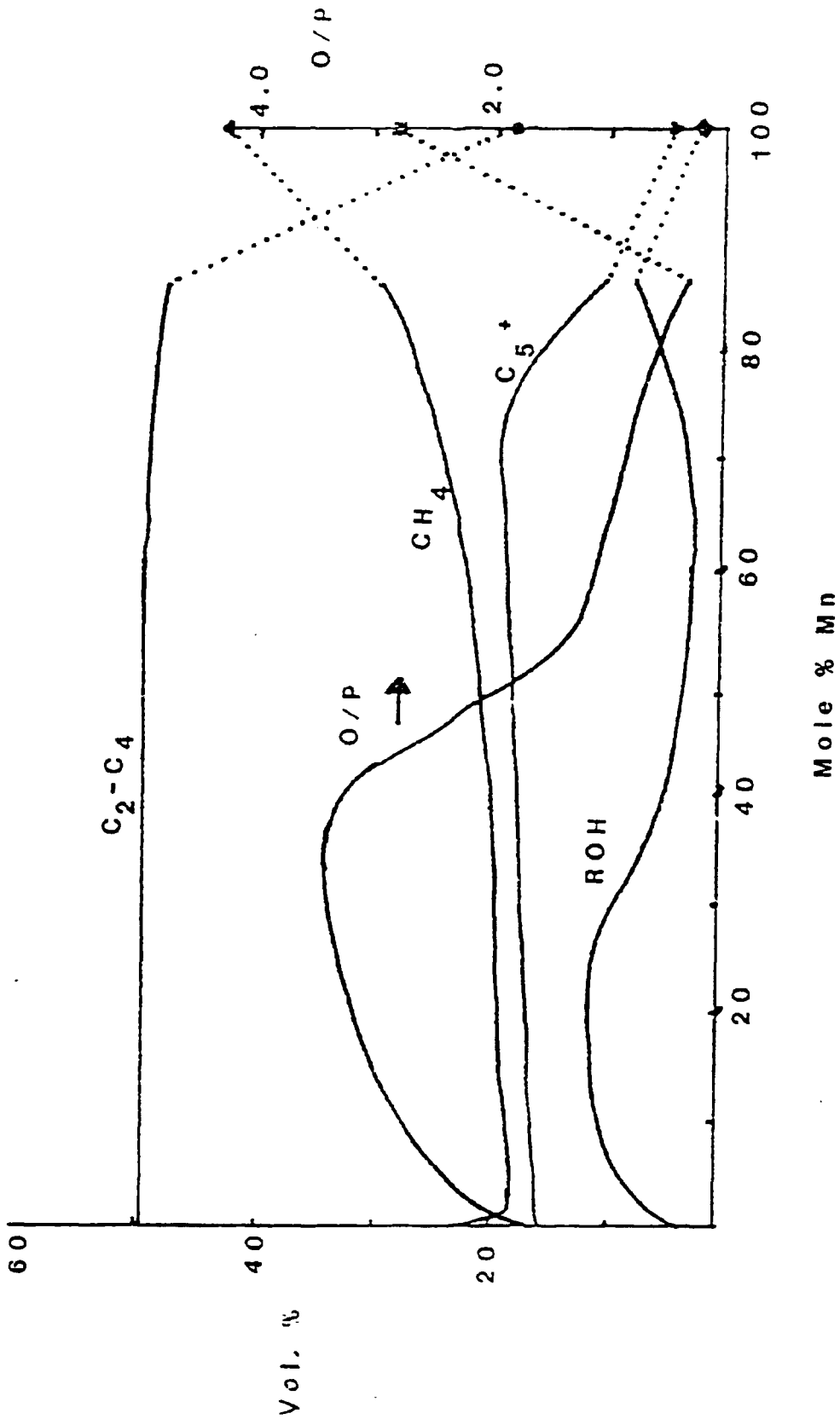


Figure 1

CHARACTERIZATION OF Fe-Mn CATALYSTS

OBJECT: DETERMINE ACTIVE PHASE(S) RESPONSIBLE FOR CATALYST SELECTIVITY

PLAN: STUDY PROPERTIES AS A FUNCTION OF CATALYST COMPOSITION

MEASURE ADSORPTION PROPERTIES

DETERMINE PHASES PRESENT

MEASURE CARBURIZATION RATES

MEASURE CATALYST ACTIVITIES FOR HYDROGENATION

DETERMINE ACTIVE STATE OF CATALYSTS IN CO + H₂

APPAR: XRD, SEM, TEM, ESCA

TEMP. PROG. DESORPTION & REDUCTION

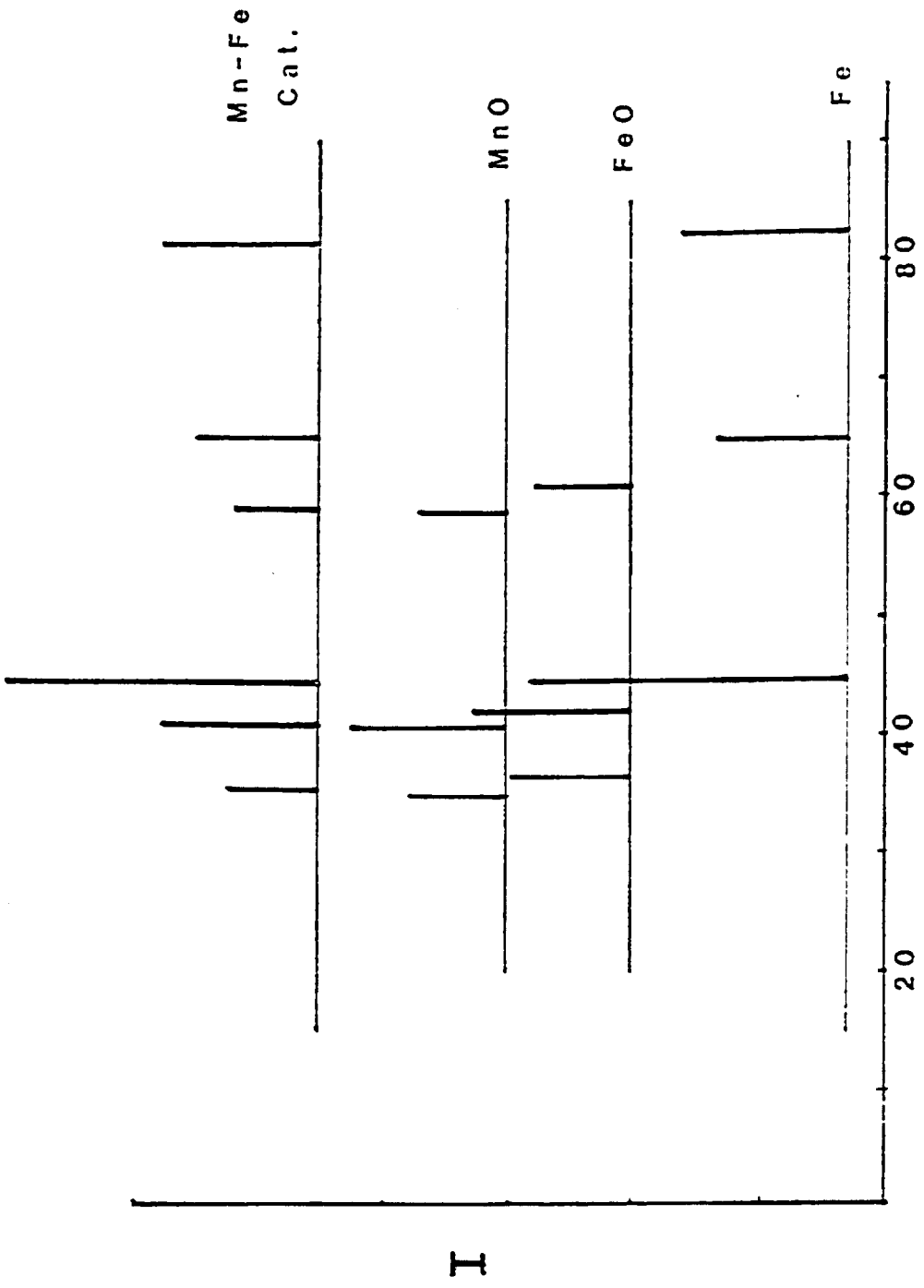
VOLUMETRIC SYSTEM

FLOW MICROBALANCE

MICROCATALYTIC REACTOR

Figure 2

XRD of Mn-Fe CATALYSTS



2θ

Figure 3

XRD OF MnO-FeO

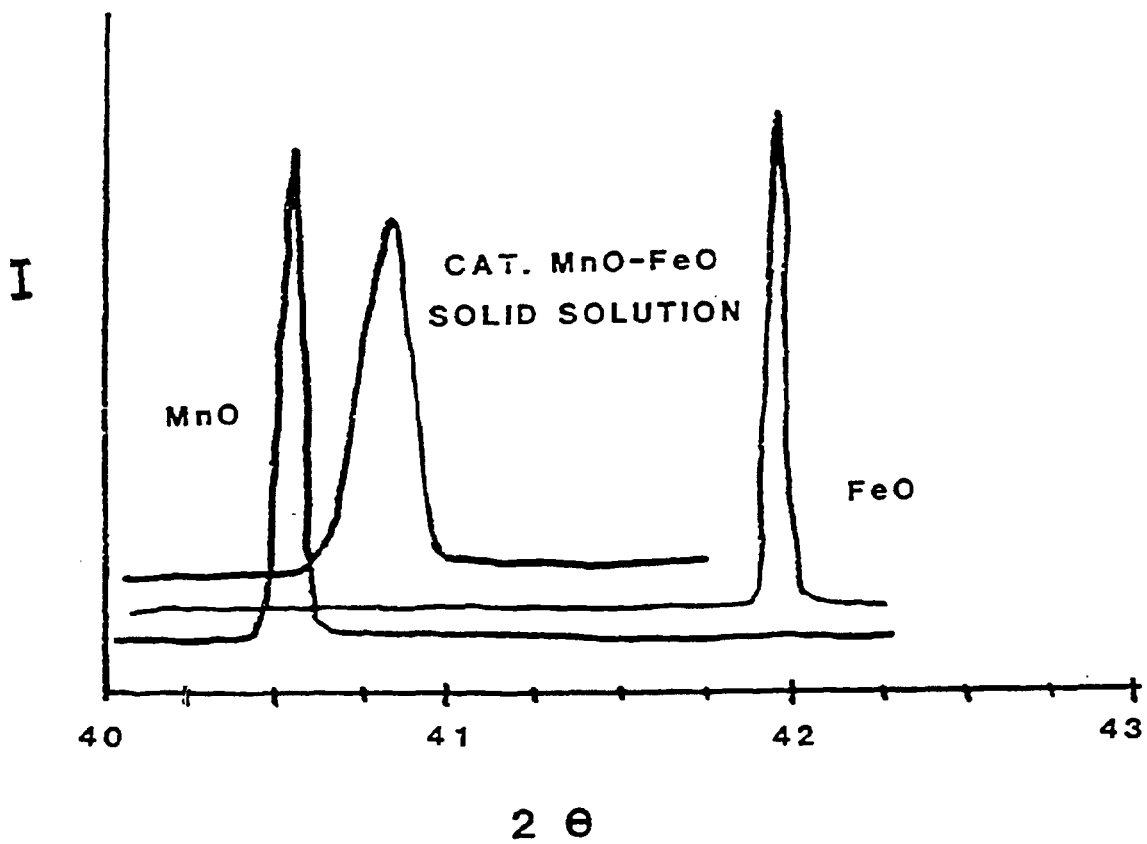
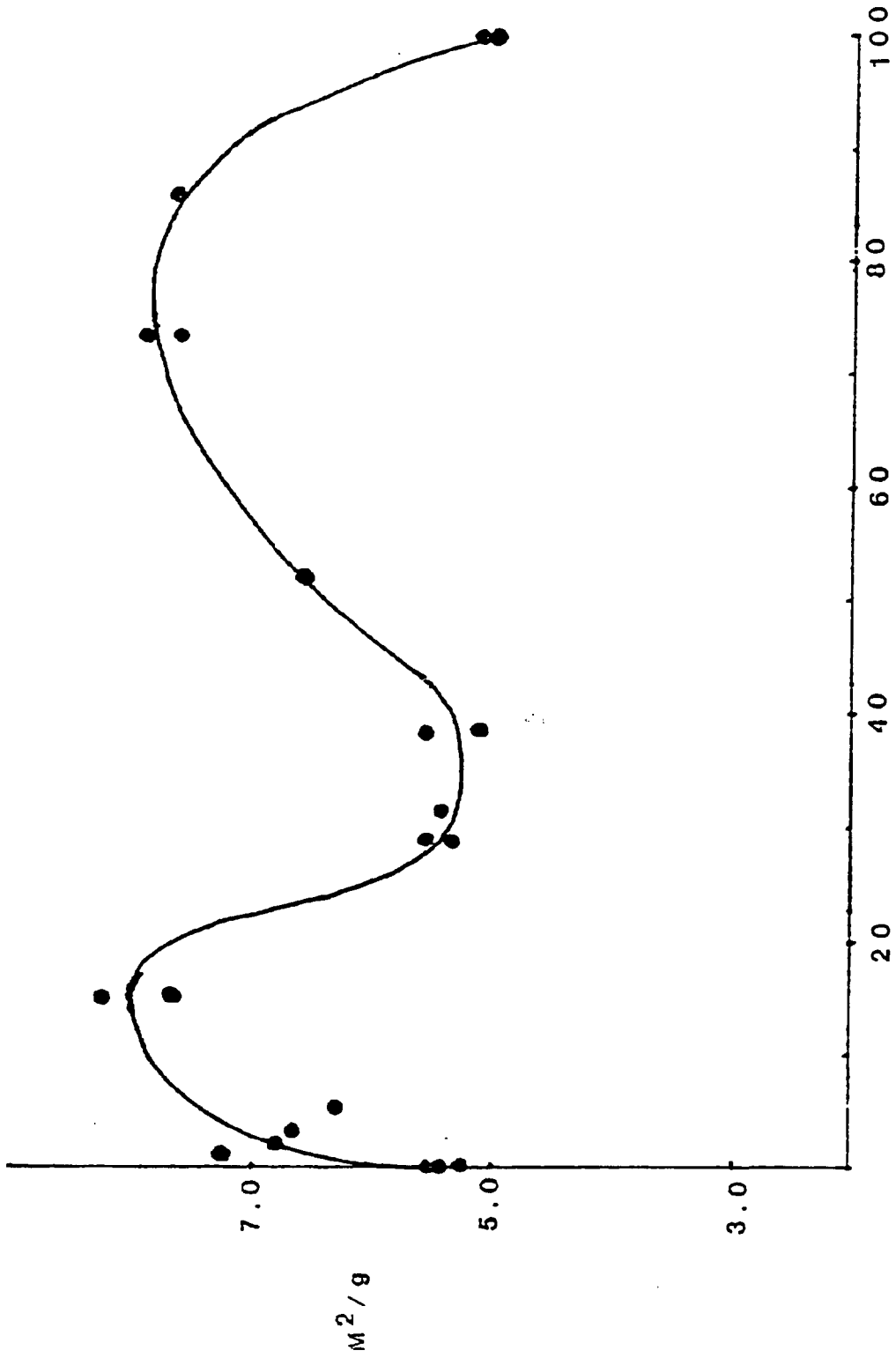


Figure 4

BET Surface Area



Mole % MnO

Figure 5

CHEMISORPTION ON Fe-Mn CATALYSTS

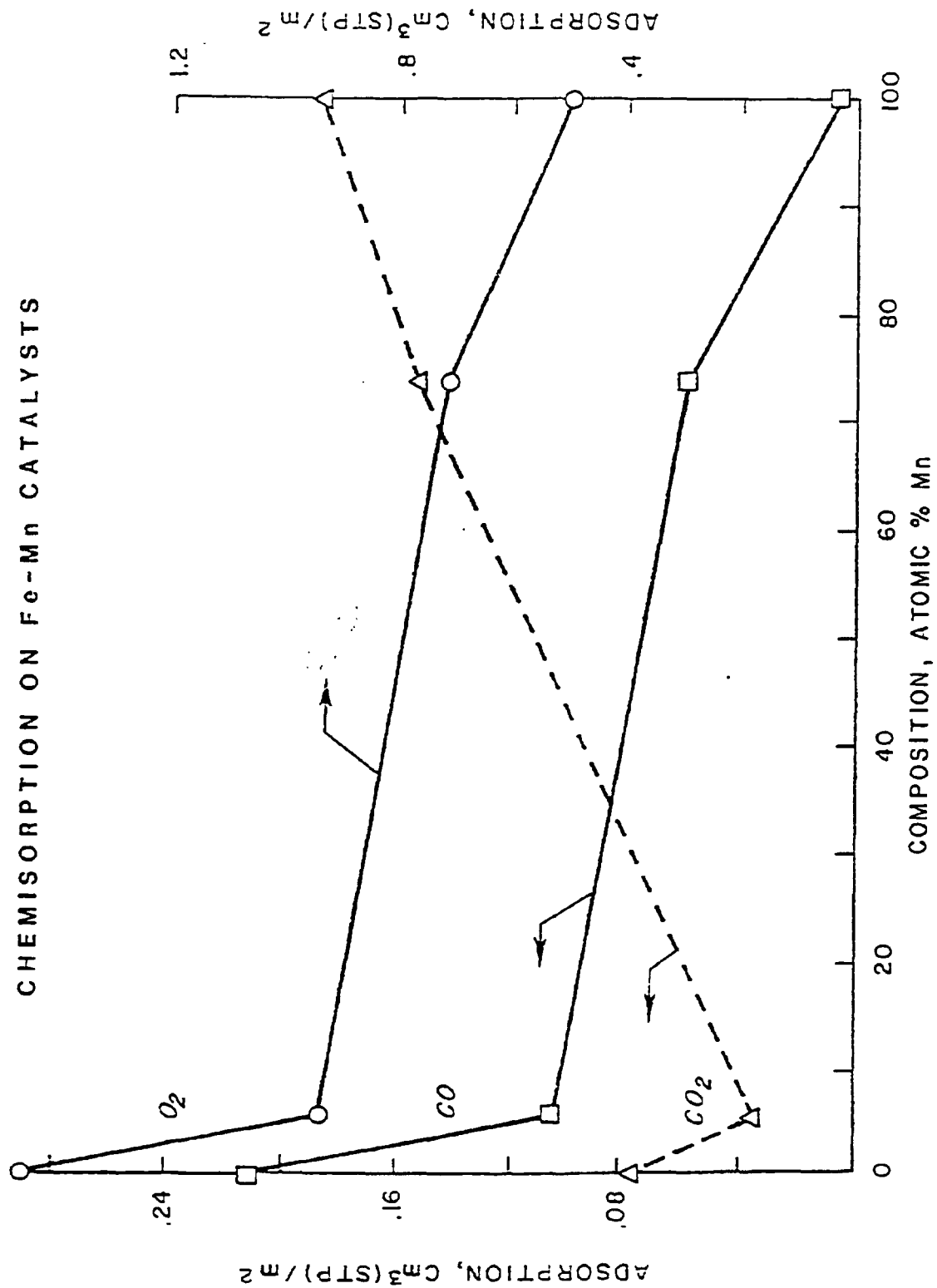


Figure 6

PROPOSED STRUCTURES

LOW Mn CATALYST (0.05)

MnO PLATELETS ON Fe SURFACE (15/1)

Fe: $d=1400\text{\AA}$

MnO: $L=560-410\text{\AA}$, $h=55-65\text{\AA}$

$f(\text{Fe}): 0.6$

HIGH Mn CATALYST (.74)

INDEPENDENT PARTICLES OF Fe AND MnO

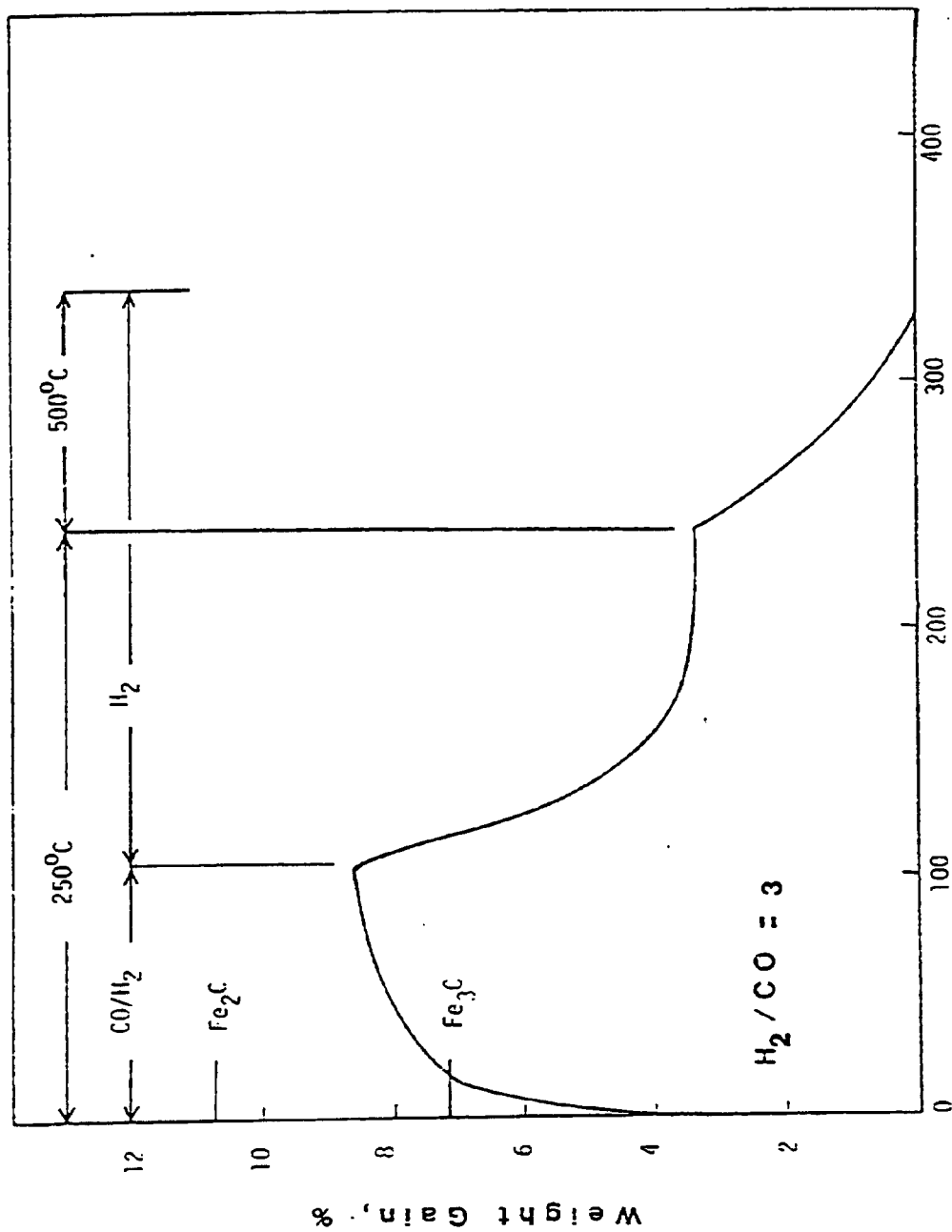
Fe: $d=800-1000\text{\AA}$

MnO: $d=1500-1600\text{\AA}$

$f(\text{Fe}): 0.4$

Figure 7

CARBURIZATION RATE FOR Fe CATALYST (C-O)



Time, Hr.
Figure 8

CARBURIZATION RATES FOR CATALYSTS C-0 & C-15

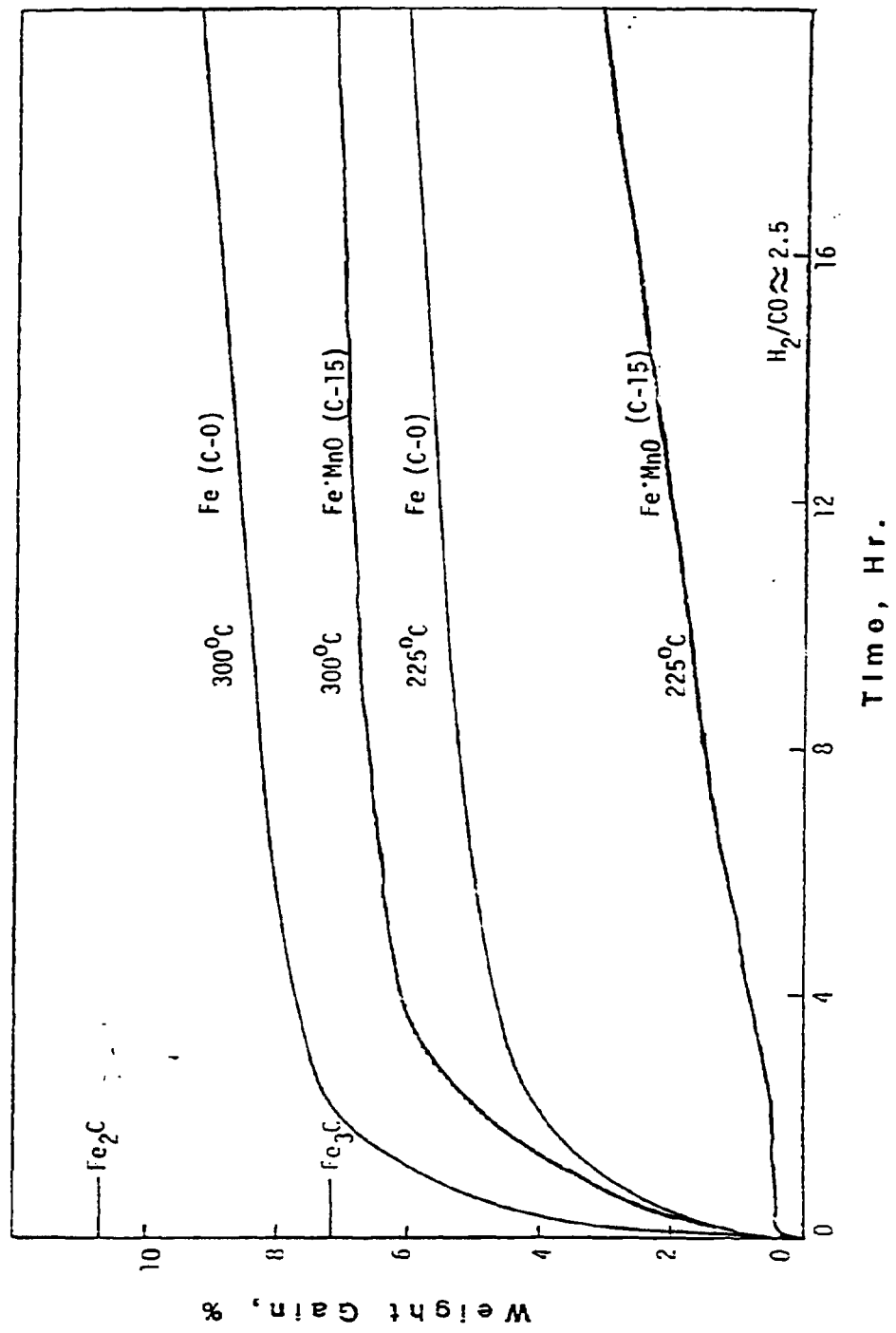
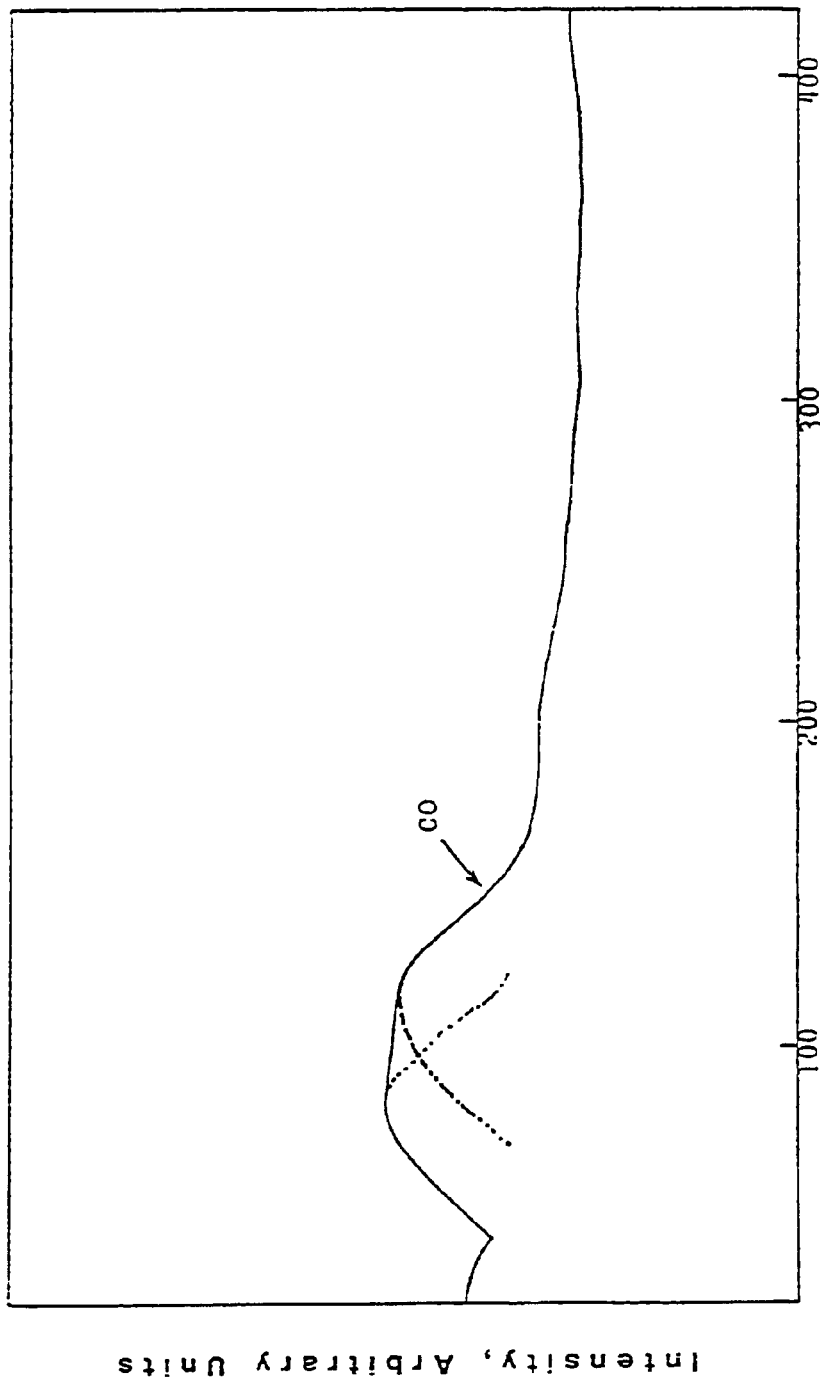


Figure 9

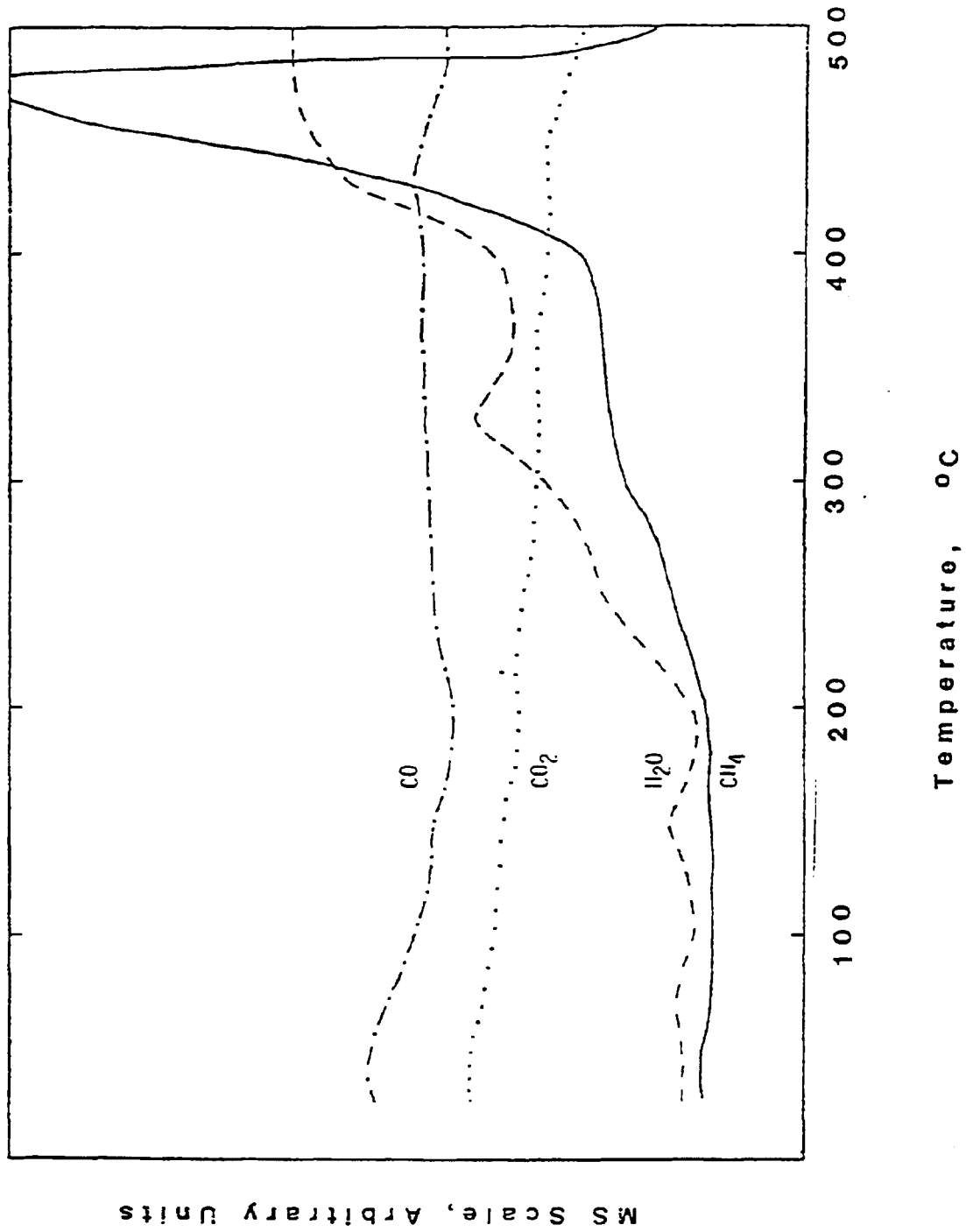
TPD in He of Preadsorbed CO on Catalyst C-15



Temperature, °C

Figure 10

TPR in H₂ of Catalyst C-5 (Step 2)



MS Scale, Arbitrary Units

Temperature, °C

TPD-TPR RESULTS

TEMP. →

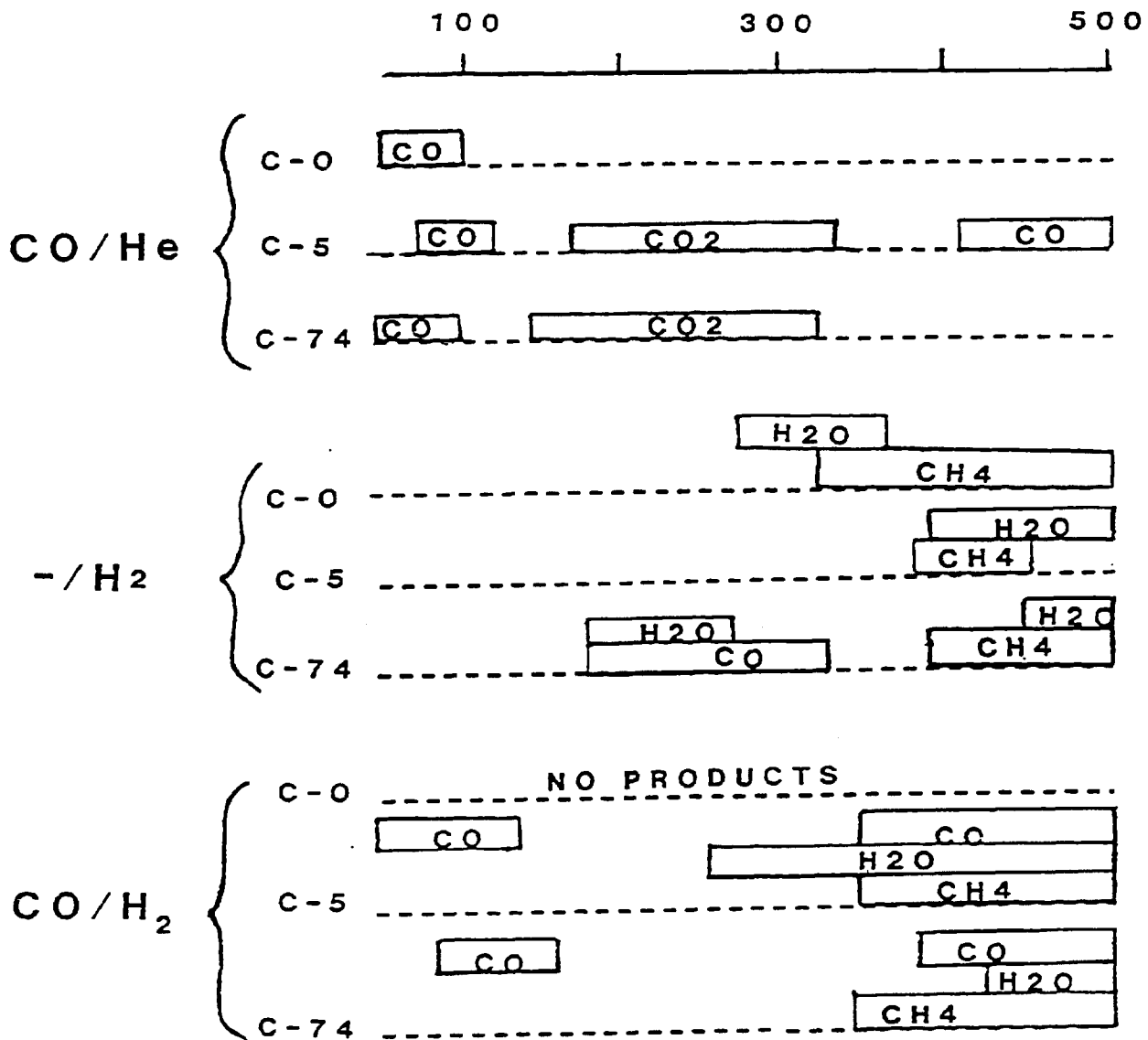


Figure 12

HEXENE HYDROGENATION ON Fe

CATALYST TREATMENT	REACTION GAS	$k_H, \text{cm}^3/\text{g min.}$		
		500C	1500C	2500C

REDUCED	H_2	-- COMPLETE CONVERSION --		
CARBURIZED #	H_2	0.4	30.5	73.3
CARBURIZED #	$2\text{H}_2/\text{CO}$	0.1	2.1	10.7

$2\text{H}_2/\text{CO}$ AT 2500C FOR 3 HR.

HEXENE HYDROGENATION Fe-Mn CATALYSTS #

Mn	Fe AREA	$k_H, \text{ cm}^3/\text{g min} (k_H^0, \text{ cm}^3/\text{m}^2\text{min})$			E_a
		1500°C	2000°C	2500°C	
MOLE %	m ² /g				kcal/mole
0	5.5	2.08 (0.38)	6.22 (1.1)	10.7 (1.9)	9
5	3.1	0.72 (0.23)	3.12 (1.0)	5.7 (1.8)	12
39	-	0.57	3.3	6.4	14
74	2.1	2.53 (1.2)	17.4 (8.3)	38.6 (18.4)	15
100	0	0.1	0.1	0.1	-

CATALYST CARBURIZED PRIOR TO
REACTION IN 2H₂/CO GAS

Figure 14