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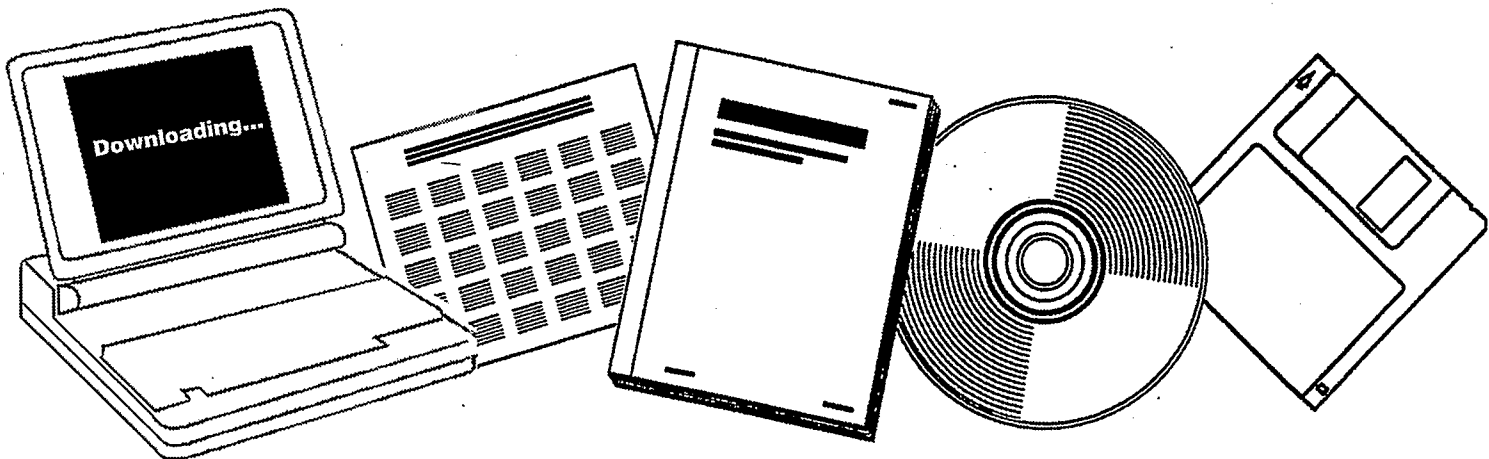
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**TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF
SYNGAS TO ALCOHOLS: THIRTEENTH QUARTERLY
REPORT, SEPTEMBER 1, 1987-NOVEMBER 30,
1987**

DELAWARE UNIV., NEWARK. CENTER FOR
CATALYTIC SCIENCE AND TECHNOLOGY

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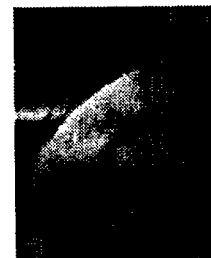
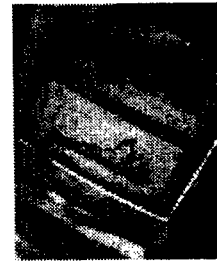
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**TRIFUNCTIONAL CATALYSTS
FOR CONVERSION OF SYNGAS TO ALCOHOLS**

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Thirteenth Quarterly Report for Period
September 1, 1987 to November 30, 1987

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MASTER

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OBJECTIVES

- Task 1. Preparation of catalyst samples
- Task 2. Testing catalysts for syngas conversion
- Task 3. Measurement of surface composition and structure
- Task 4. Determination of nature of surface complexes
- Task 5. Reaction mechanism determination by isotopic tracers and kinetics
- Task 6. Design, prepare and test optimized catalysts

ABSTRACT

In this quarter, the problem of separation of the reaction kinetics for carbon monoxide hydrogenation for the synthesis of primary and secondary products was investigated for molybdena modified rhodium/alumina catalysts. A new mathematical method (Delplot) for separating primary/secondary products was found. The utility of this approach is in the easy method of finding the effect of process parameters (GHSV, CO/Hydrogen, Pressure) on the reaction pathway. Furthermore, this method is used to separate regimes of space time (conversion) where a certain product is primary or secondary.

The results of the ongoing investigation of particle size and spatial distribution of various components using TEM and XRD are discussed.

Task:3 Measurement of surface complexes

Task:4 Determination of nature of surface complexes

Task:5 Reaction mechanism determination by isotopic tracers and kinetics

Separation of Kinetic Primary/Secondary Products

Introduction

Separation of products into primary and secondary groups is essential to the investigation of the kinetics and performance of the catalysts. A kinetic primary product is one which is formed from one slow step while a kinetic secondary product is formed from several slow steps. A brief analysis of this method for Rh-Na/Al₂O₃ catalysts was given in the sixth quarterly report. In this section a detailed analysis of this method and its application for Rh-Mo/Al₂O₃ catalysts is discussed.

Previously two different methods were used to separate primary and secondary products. In the first method, which is also known as the initial rate method, the rate of formation of a product is plotted against space time. A positive slope indicates that the product is primary, while a zero slope indicates that the product is secondary. This method needs differential reactor data. In the second method the rate of formation of a product is plotted against the total flow rate at a fixed partial pressure of the reactants. A finite asymptotic value of rate at large flowrates indicates a primary product.

An improvement over the generally used differential method based on initial rates is to plot (mole fraction of product/ conversion of A) against conversion of A. If product P is secondary, the y-intercept is zero but if product P is primary, it has a finite intercept. In the case of primary products the intercept is a ratio of pseudo first order rate constant of the slowest step leading to the formation of product P to the sum of pseudo first order rate constant leading to the formation of various other products. Furthermore, based on the kinetics of each step, the intercept can vary with the initial concentration (partial pressure) of the reactants, except when all reactions are first order. Using the above method it is

possible to separate the reaction network into distinct regimes where a species is a kinetic primary product and kinetic secondary product.

The advantage of the method described is two-fold. Firstly integral kinetic data can be used. Secondly a lot more information can be obtained from the intercepts. To understand this, lets see how this method works.

$$\text{Intercept} = \lim_{\tau \rightarrow 0} B \left(\frac{1}{A_0 - A} \right)$$

$$\text{Intercept} = r_P^0 \left(\frac{1}{\sum_{i=0}^n r_A^0} \right)$$

where

r_P^0 is the initial rate of species P

and n is the number of steps in which A is consumed

If Intercept = 0 then product is non-primary and if intercept \neq 0 then product is primary.

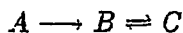
Hence the intercept for a primary product is the ratio of the pseudo first order rate constant in the slowest step leading to the formation of that product divided by the sum of pseudo first order rate constants of all slow steps by which the reactant is consumed. Thus by finding the intercepts at various partial pressures of the reactants we can find how the reaction pathway changes with partial pressure of the reactants. As an example, figure 1 illustrates the use of such a plot for Rh-Mo/Al₂O₃ catalysts. We have not only used this method to for separating kinetic primary and secondary products but also extended it further to separate them into regimes, i.e. into regimes where a certain product is primary and regimes where certain product is secondary.

In figure 2, the molefraction of MeOEt/Conversion is plotted against the conversion of CO. The figure can be divided into two asymptotic regions. In region 1 the time constant τ_2 is less than τ_c .

In the reaction of CO and H₂ over 3%Rh 7.5%Mo/Al₂O₃ the finite intercepts for MeOH, MeOMe and CO₂(figure 1) show that the products are primary as is CH₄. The results indicate that there is only one slow step in the formation of the above products. This implies that either MeOH or MeOMe is formed from the same intermediate on the surface and the formation of the intermediate is the slow step, or the conversion of MeOH to MeOMe is very fast. The finite intercept for CO₂ implies that the water gas shift reaction is very fast so that water reacts with CO to form carbon dioxide as soon as it is formed.

Table 1 lists the intercepts of CO₂, MeOH and MeOMe for 3%Rh 7.5%Mo/Al₂O₃ as a function of CO/H₂ ratio. The intercept for carbon dioxide decreases with decrease in CO/H₂ ratio because the gas phase contains more hydrogen and hence the water gas shift reaction is less favored. Higher amounts of MeOH are formed at higher H₂/CO ratio and this leads to a higher intercept.

In the case of formation of MeOEt (figure 2.), two distinct regimes are seen. MeOEt is a primary product above 1.5% CO conversion, while it is a secondary product for low conversions. Regime 1 consists of low conversion or low space time runs, while regime 2 consists of high conversion or high space time. The above behaviour can be explained by considering the following example.



Let τ_1 and τ_2 be the time constants for each reaction step. Usually $\tau_2 \ll \tau_c$, where τ_c is the space time. This leads to the second step being at equilibrium and hence C is a kinetic primary product. In the case where $\tau_2 \gg \tau_c$, the molecules do not have enough time to equilibrate according to reaction 2. This leads to two slow steps in the formation of C, hence C is a kinetic secondary product. The point of change in the regimes gives an order of magnitude estimate of τ_2 , which is O(8 sec) for MeOEt.

Transmission Electron Microscopy (TEM)

Introduction

Transmission electron microscopy was used to find particle size and distribution of various components on the catalyst surface. Scanning transmission electron microscopy (STEM) with energy dispersive x-ray analysis (EDX) was used in conjunction with TEM to find spatial element distribution. A Phillips EM 400 electron microscope with attached STEM/EDX unit was used. Fresh and used catalysts were used. The sample preparation included grinding the sample on glass slide. Small particles of sample were then transferred to the copper grid. To get meaningful and comparable data, experiments were run on the same catalysts used in reaction and characterization studies. It is difficult to get good contrast from porous supports. This is because of the many vacuum-support interfaces present in the beam path in the specimen. This results in large scattering of the electron wave from the support. The porous catalyst alumina used consists of small crystalline particles in the range of 10 to 100nm. The small crystallite size of the alumina particles and its semi-crystalline nature decreases the contrast further. Fresh and used catalysts such as Rh/Al₂O₃, Mo/Al₂O₃ and Rh-Mo/Al₂O₃ did not show any particles. XRD studies on fresh and used catalysts did not show any detectable pattern of Rh or Rh-oxide. To make sure that the operating procedure was right Rh/MgO used catalysts were also run.

Figure 3 and 4 show electron micrographs of 3% Rh 15% Mo/Al₂O₃ and 3% Rh/Al₂O₃. From the figures it is clear that there is insufficient contrast. Figures 5 and 6 show the energy dispersive x-ray analysis spectrum obtained from the regions shown in figure 3 and 4. The spectra shows the presence of rhodium and molybdenum in the specimen. Intense Cu peak is from the grid and the specimen holder.

Diffraction patterns of the gamma alumina supported sample do not show any features. This is because of the very small particle size and the semi-crystalline nature of the support.

In the case of magnesia supported Rh catalysts. The bright field images do not show any distinct contrast even upto 480K magnification. Figure 7 shows bright field images of Rh/MgO used catalysts.

Yacaman et al. [1] have shown from dynamical theory calculations that the particle-support contrast for a dark field images is high compared to bright field images. These calculations were carried out for non-porous support, however the conclusion still hold for porous supports. This is the reason we tried dark field method. The diffraction pattern of Rh/MgO used catalysts consists of rings and spots. Since the predominant spacing for MgO and Rh is nearly same, the diffraction spots or arcs arising from Rh and MgO are at the same radial distance. Figure 8 shows the diffraction pattern of Rh/MgO crystals. The sample is tilted to give the highest intensity in the diffraction pattern. Figure 9 shows the dark field image of Rh/MgO when the objective aperture is on the 2 o'clock spot in the diffraction pattern.

The particle size measured from the dark field image is 200Å. XRD pattern show Rh particles in used catalysts (figures 10 and 11). The rhodium particle size as measured from x-ray line broadening experiments was 150Å. However the MgO peak corresponds to a crystallite size of 200Å. Further experiments are underway using STEM/EDX to analyze the elemental composition of the particles which give rise to the contrast.

TEM investigation on the alumina supported molybdena catalysts will be continued at University of New Mexico in collaboration with Professor Abhaya K. Datye.

References:

- 1: M. Jose Yacaman and J.M. Dominiguez, J.Catal.1981, 67, 475.

SEPARATION OF PRODUCTS

CO hydrogenation on 3%Rh7.5%Mo/alumina
225C, 30 atm, Hydrogen/CO=2

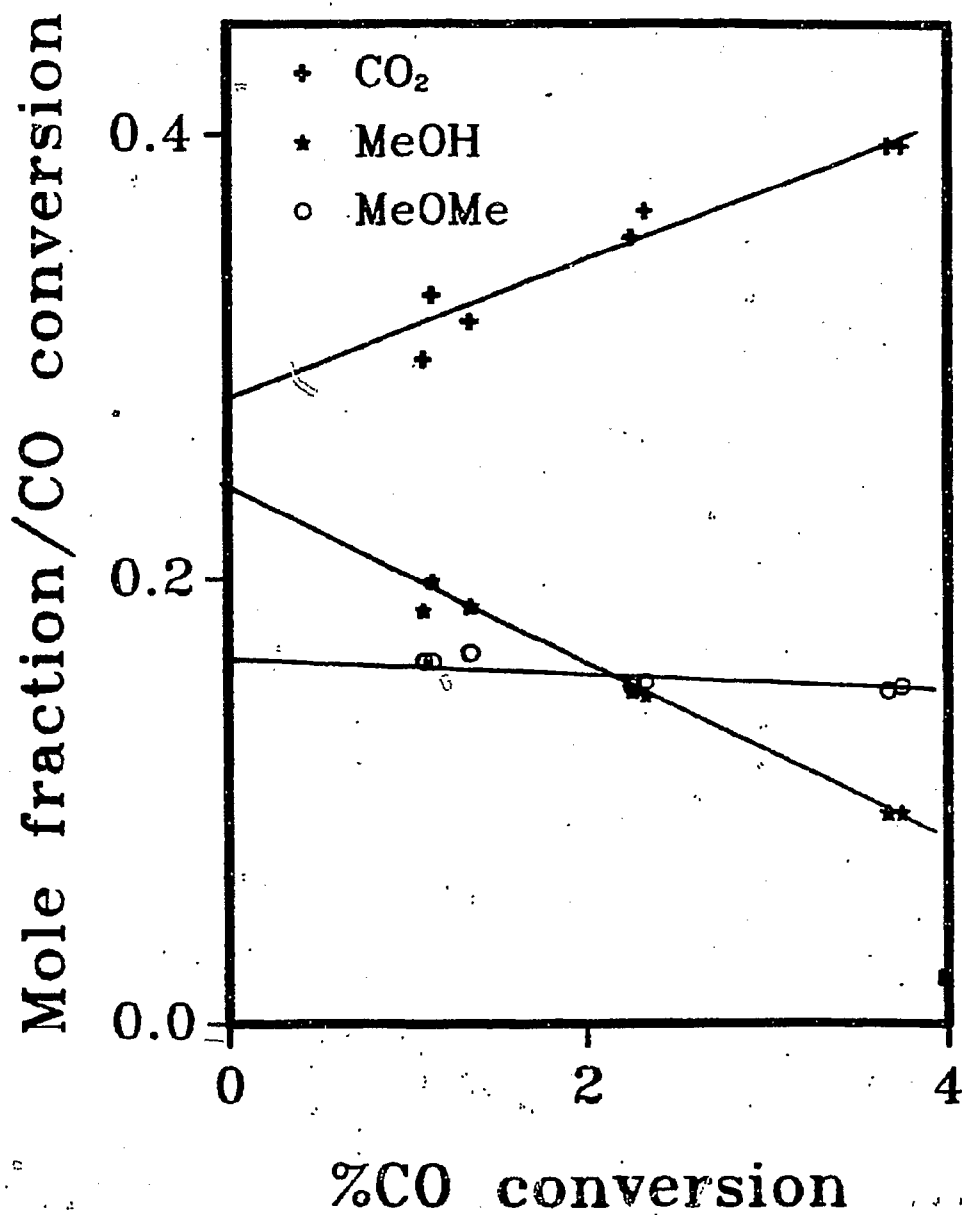


Figure 2

SEPARATION OF REGIMES Primary/Secondary Products

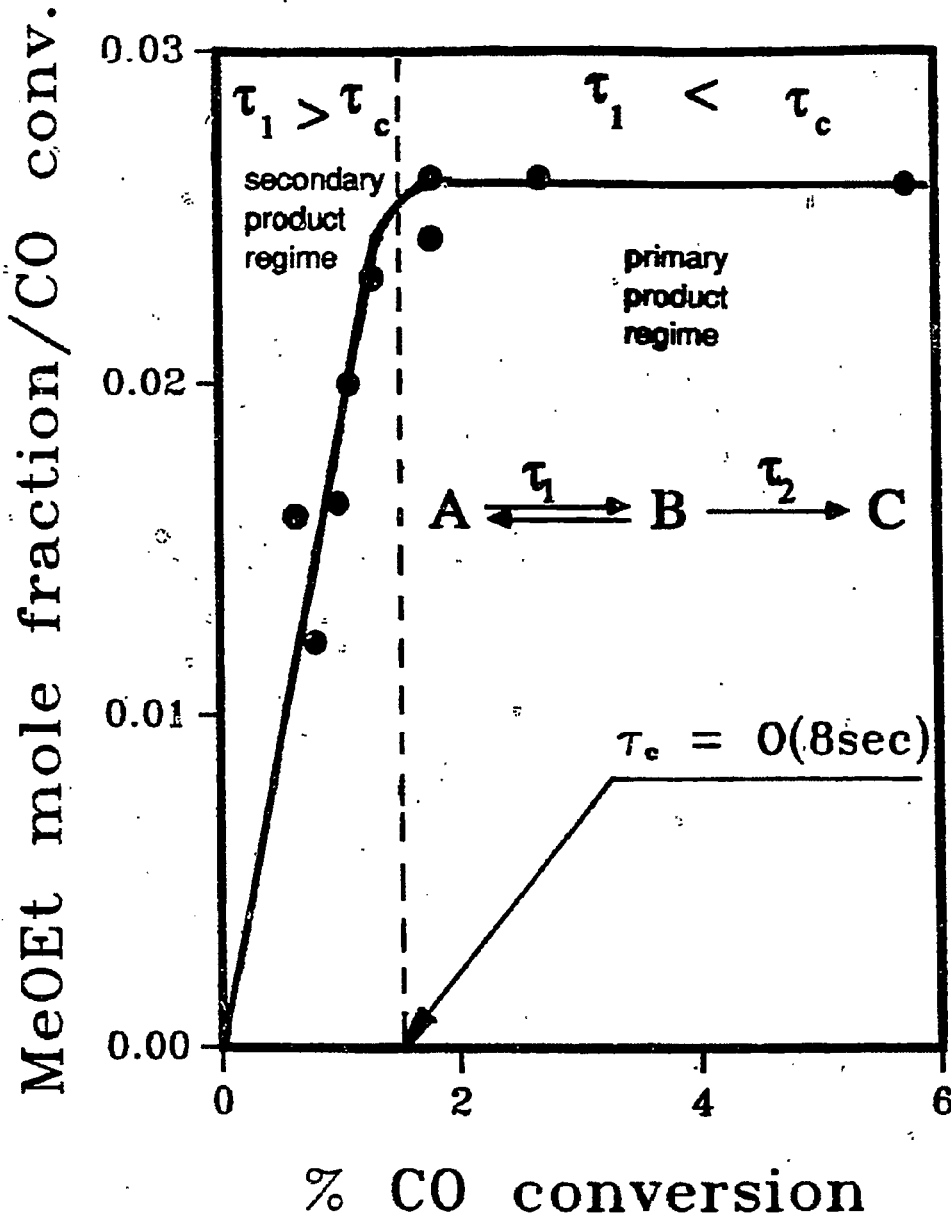


Figure 3: Transmission Electron Micrograph of
3%Rh/Alumina used

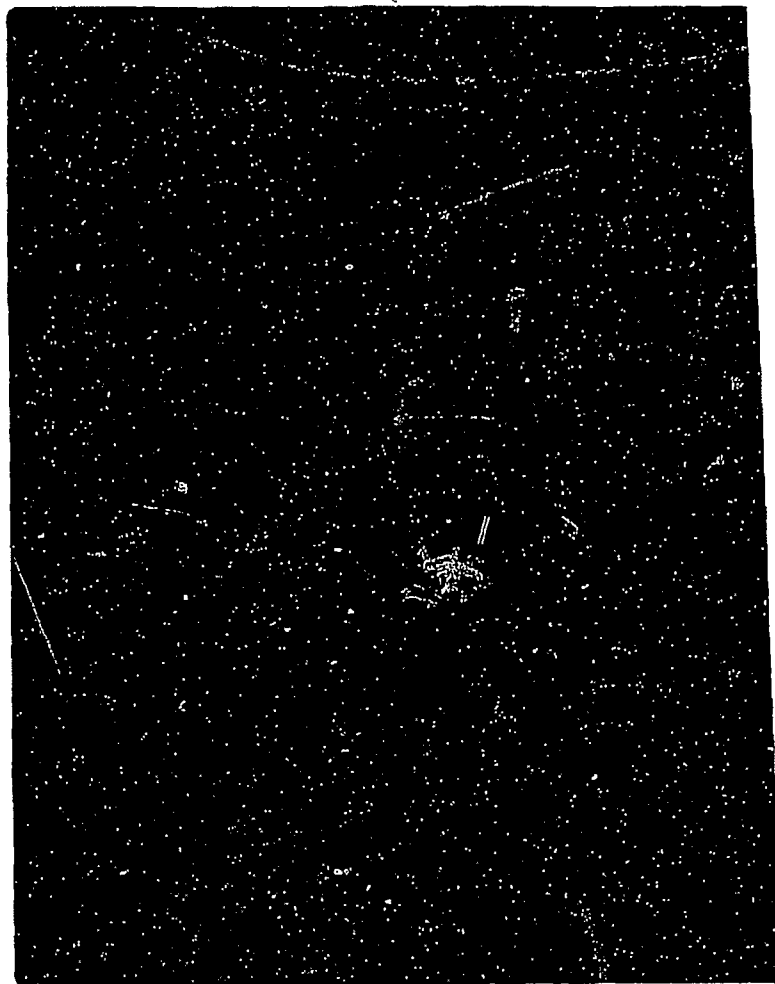


Figure 4: Transmission Electron Micrograph of
3%Rh 15%Mo/Alumina-used



Figure 5: Energy Dispersive X-ray Analysis
of 3%Rh/ALumina -used

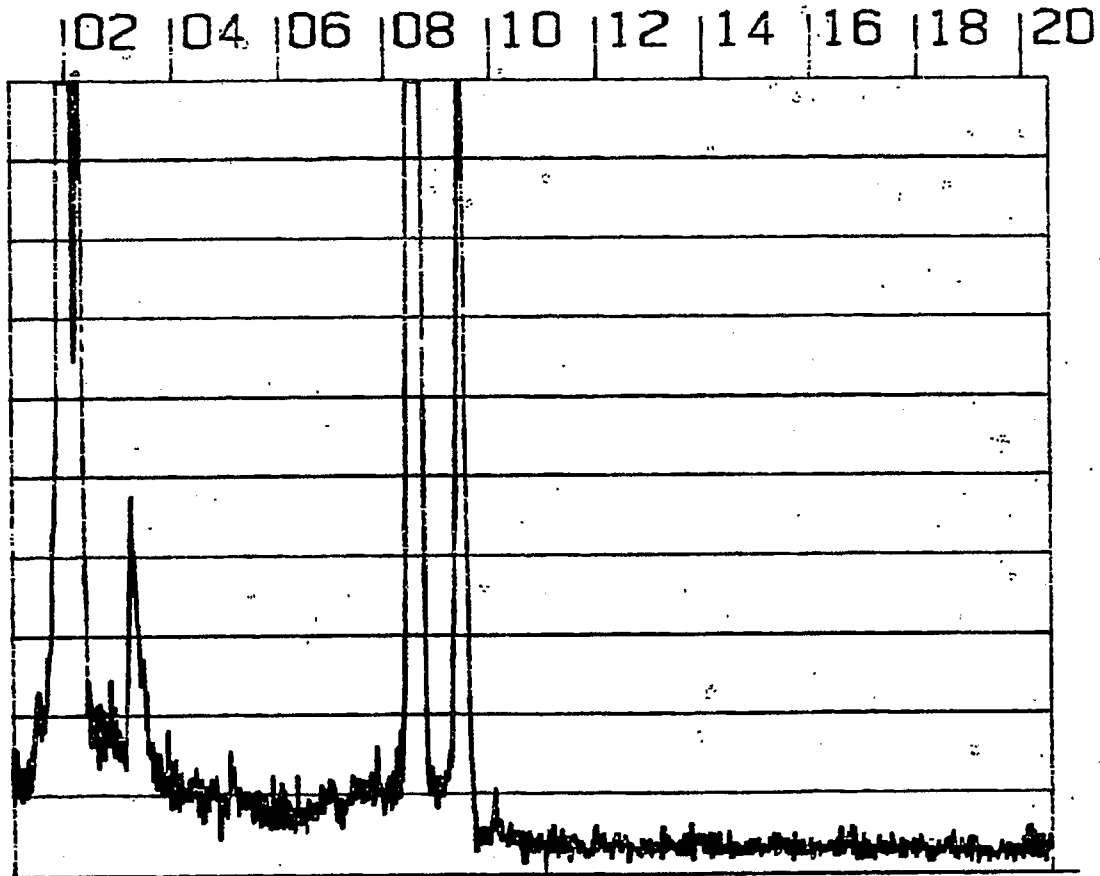
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RATE: CPS TIME 100LSEC

00-20KEV: 10EV/CH PRST: 100LSEC

A: 3%RH/AL2O3CAL2B:

FS= 409 MEM: A FS= 12



A R
L H

C
U

CURSOR (KEV) = 10.480

EDAX

Figure 6: Energy Dispersive X-ray
Analysis of 3%Rh15%Mo/Alumina-used

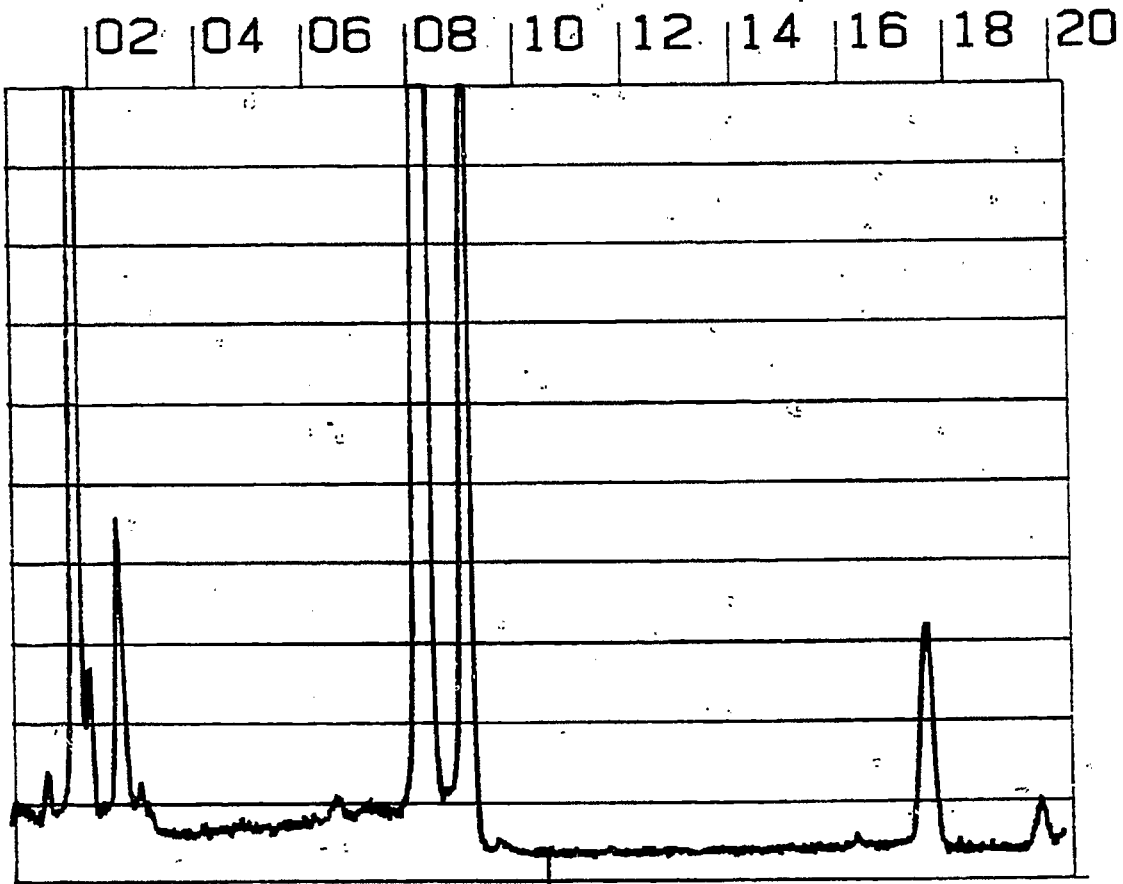
21-DEC-87 10:15:50

RATE: CPS TIME 400LSEC

00-20KEV: 10EV/CH PRST: OFF

A: RM15CALC108-98B:

FS= 4287 MEM: A FS= 25



A R
L H

C
U

M
O

CURSOR (KEV) = 10.240

EDAX

Figure 7: Transmission Electron Micrograph of
3%Rh/MgO used

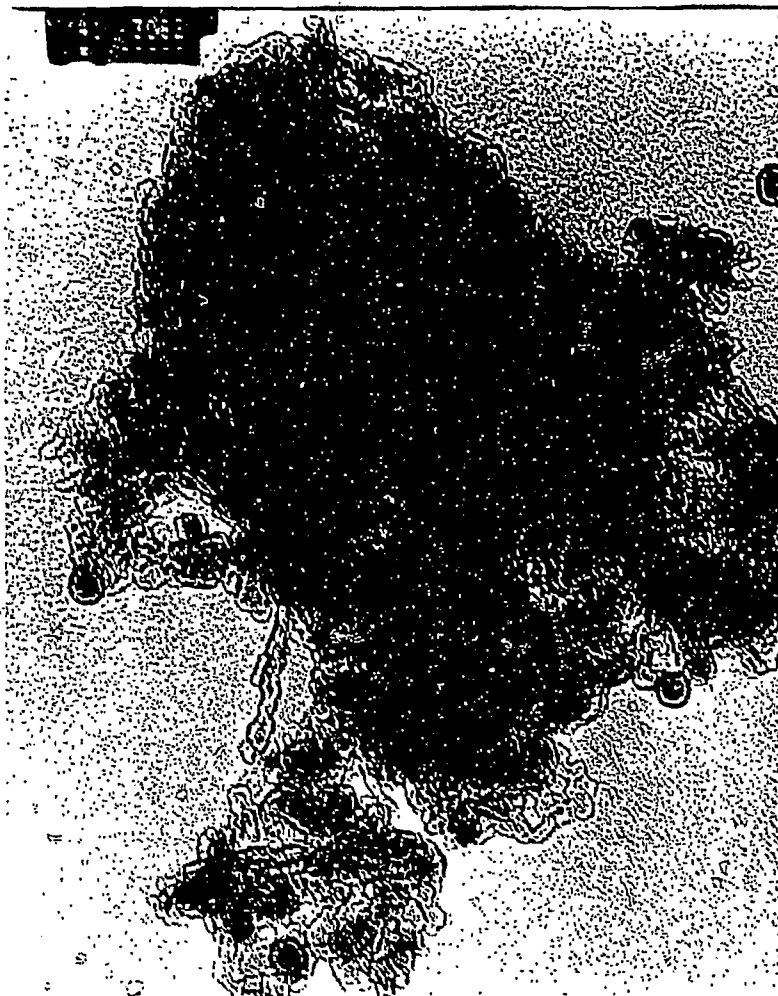


Figure 9: Non-centered Dark Field Micrograph of 3%Rh/MgO used catalyst

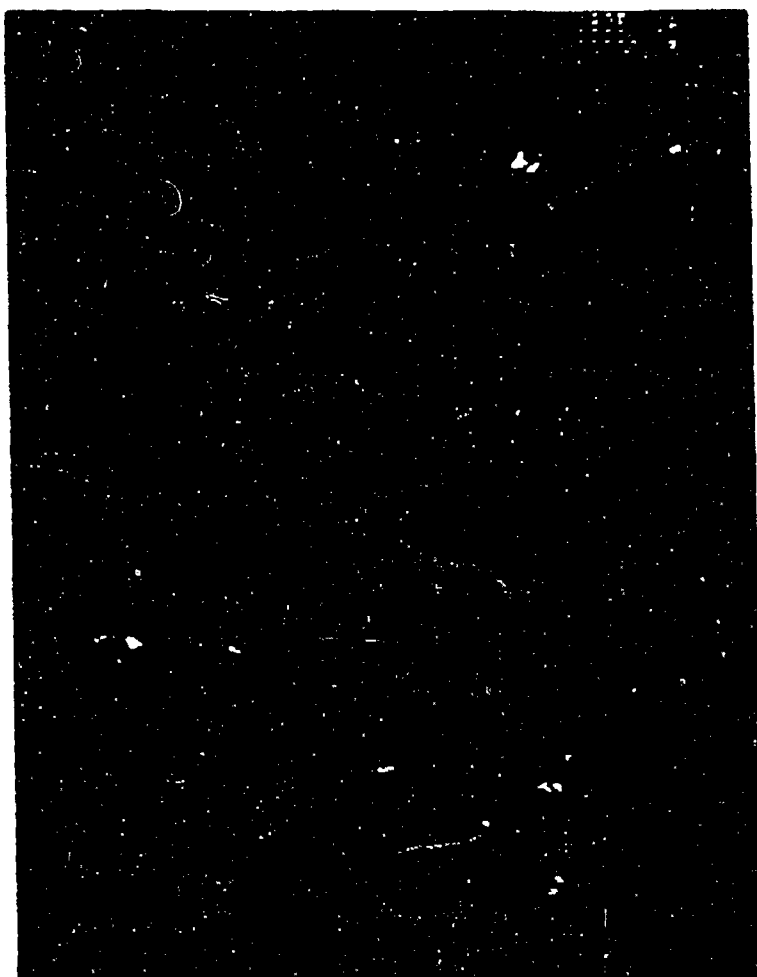
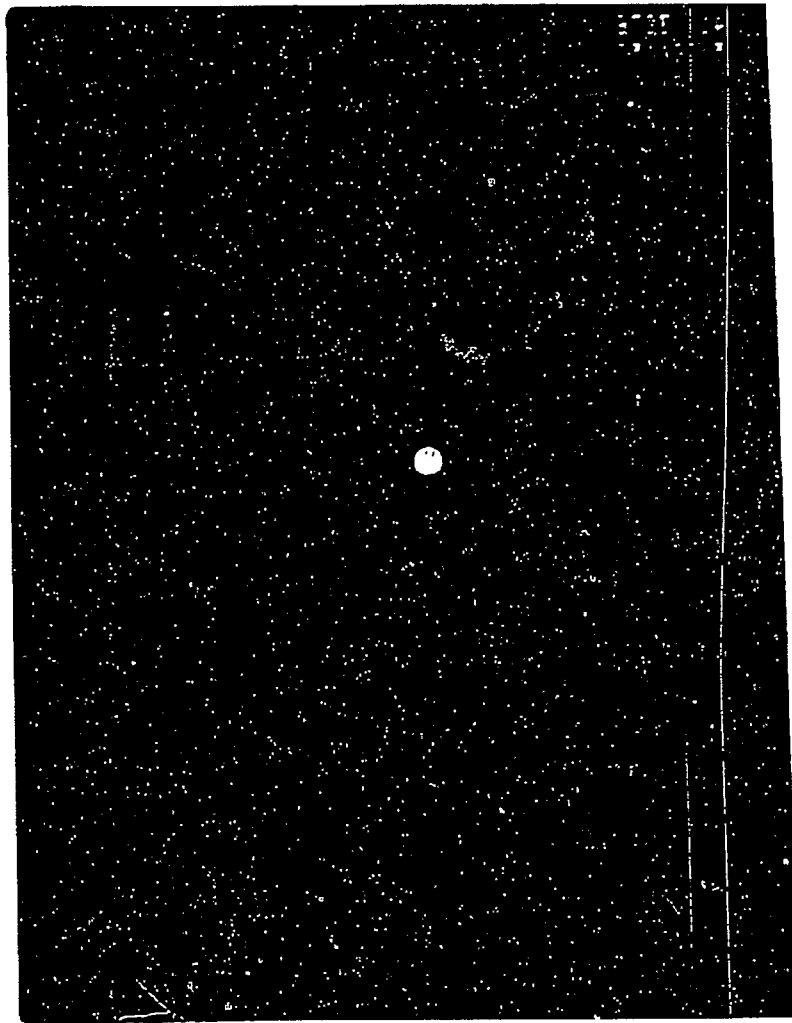


Figure 8: Electron Diffraction Pattern of
3%Rh/MgO used catalyst



X-Ray Diffraction

Figure 10

3%Rh/MgO Used Catalysts 53-83;108-100

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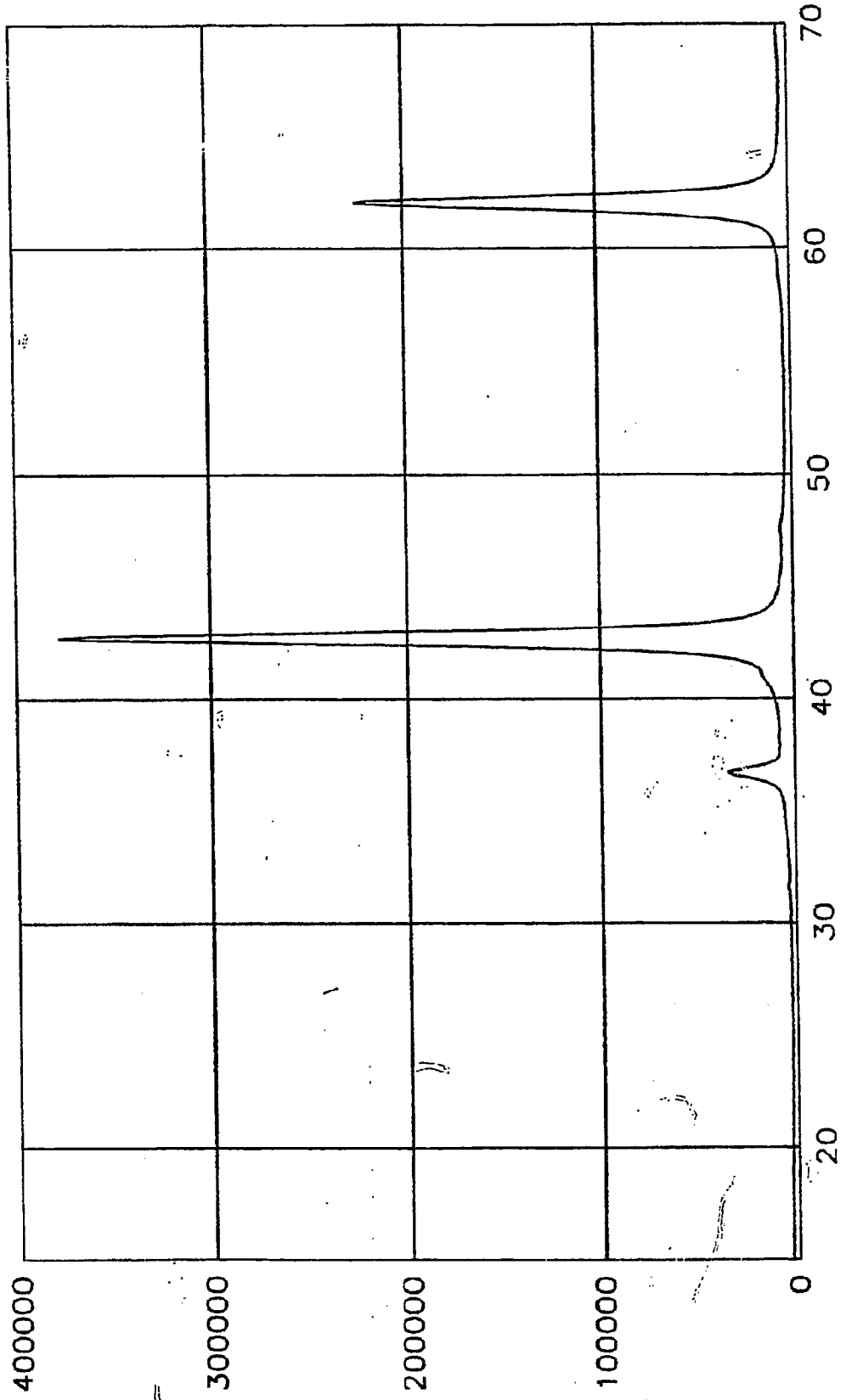


Figure 11

X-ray Diffraction

Rh/MgO Used catalysts

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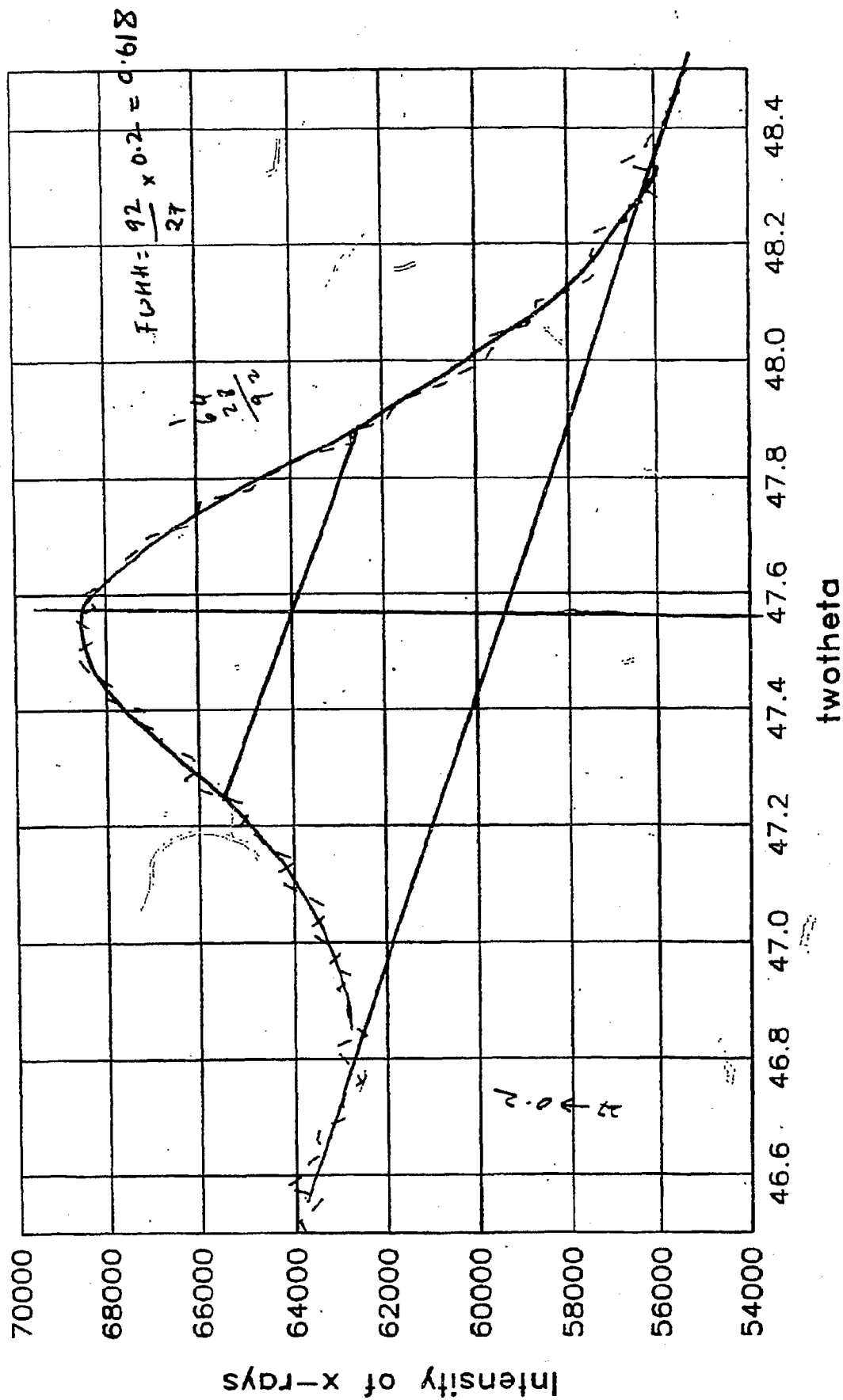


Table 1

Intercepts from Delplot

CO/H ₂	pCO psi	pH ₂ psi	Intercepts		
			CO ₂	Intercept MeOH	MeOMe
2	300	150	0.27	0.24	0.17
1	225	225	0.21	@	@
1/2	150	300	0.1	0.3	@
1/3	112.5	337.5	0.09	0.40	0.15
1/5	75	375	0.06	0.43	0.13

@ - very small, cannot be accurately found

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