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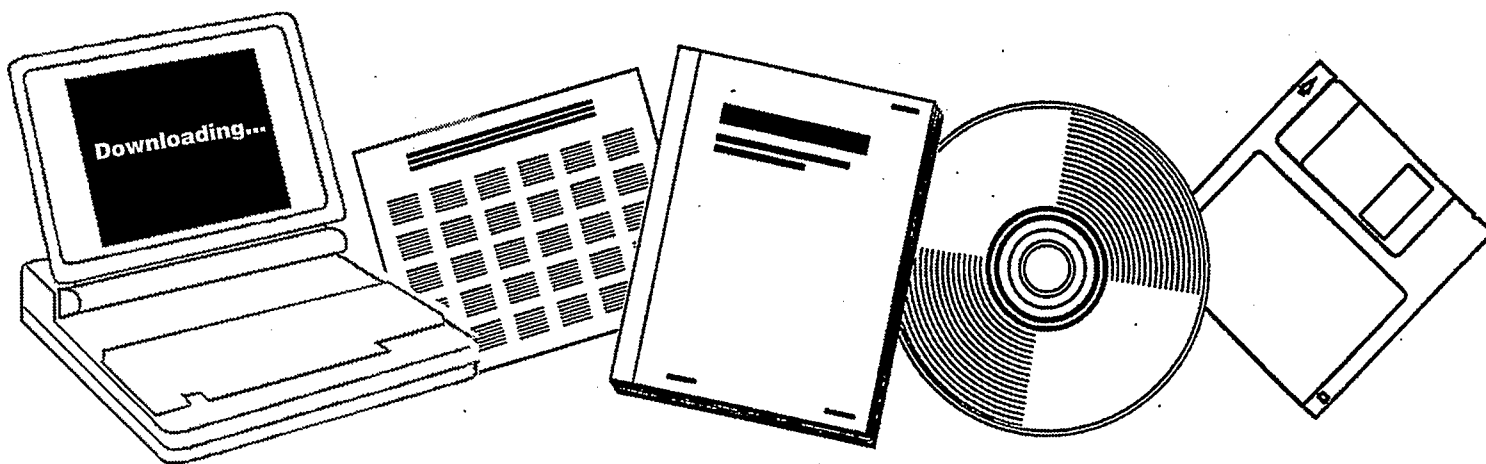
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**TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF  
SYNGAS TO ALCOHOLS. THIRD QUARTERLY  
REPORT, MARCH 1-MAY 31, 1985**

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

11 JUN 1985



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### TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

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Third Quarterly Report for Period  
March 1, 1985 to May 31, 1985

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#### OBJECTIVES

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

## ABSTRACT

An exploratory series of prepared and purchased rhodium catalysts have been tested for CO hydrogenation with interesting results. The results are summarized in the following table for typical test conditions, 250° C, 30 atmospheres pressure, 2 H<sub>2</sub>/CO at 4000 GHSV.

TABLE I	%CONVERSION	%OXYGENATES	%C <sub>2</sub> +OXYGENATES
3% Rh-Al <sub>2</sub> O <sub>3</sub>	6	33	75
" " +0.67% Na or 1%K or 1%Mn	2.5	33	75
" " + 2% Na	1	65	60-70
2.5% Rh-0.3%Mn-0.3%Mo-SiO <sub>2</sub>	6	65	90
3% Rh-1%Mn-1%Mo- SiO <sub>2</sub> /MgO (florisil)	1	87 only MeOH and EtOH	35
5% Pd-Charcoal (Aldrich)	2.3	100 all MeOH	0

Rhodium-alumina catalysts are moderately active, eg 6% CO conversion. Selectivity of CO to oxygenates is typically 30% with the balance mostly methane. An important feature is that 75% of the oxygenates are C<sub>2</sub>+, including ethanol, acetic acid and methyl and ethyl acetates.

The addition of sodium or potassium lowered the activity considerably. However for the highest Na level tested, (2%wt.Na) selectivity to oxygenates increased to 55-75%, though CO conversion was only about 1% to 2.5%.

The addition of 1% Mn to Rh-Al<sub>2</sub>O<sub>3</sub> decreased activity with no increase in selectivity. A higher Mn loading decreased activity further without affecting selectivity. This is quite contrary to previous observations on the effect of Mn on SiO<sub>2</sub>-based Rh catalysts.

Two catalysts containing SiO<sub>2</sub> gave relatively high selectivity. One, a Rh-Mn-Mo-SiO<sub>2</sub> catalyst, similar to the Van den Berg catalyst, gave 6% conversion and 50 to 70% selectivity to oxygenates.

Another catalyst, Rh-Mn-Mo- Florisil (SiO<sub>2</sub>-MgO), gave the highest selectivity found so far, 93%, though at low conversion.

A Pd-active carbon catalyst produced only methanol ( no CH<sub>4</sub> nor C<sub>2</sub> H<sub>5</sub>OH).

The above catalysts now provide a basis for experiments relating composition to performance, to provide samples for study by instrumental techniques, and to provide a rational basis for additional catalyst preparations.

### Tasks 1 and 2. Catalyst Preparation and Testing for Syngas Conversion.

A series of rhodium-containing catalysts was prepared and tested. In general, the preparations were by no-excess impregnation of the support using nitrate solutions of rhodium and modifiers. Following air drying and calcination at 500°C, the catalyst was cooled and reduced in flowing H<sub>2</sub> at increasing temperatures to 500°C.

Testing for syngas conversion was carried out in the flow reactor system, previously described, at 225, 250 or 275°C, and for the most part, at pressures of 30 or 50 atmos. and a H<sub>2</sub>/CO ratio of 2. The flow rate was varied, but usually corresponded to 4000 GHSV.

Certain problems were encountered initially. A heated charcoal filter in the purification line was found to be emitting CO<sub>2</sub> and H<sub>2</sub>O resulting in analytical uncertainties. This was corrected by replacing the charcoal with alkalized alumina.

Furthermore, the first series of catalysts ( 3% Rh on Al<sub>2</sub>O<sub>3</sub> with and without added Na or K ) all proved to be essentially inactive. These catalysts were all prepared using a solution made up from pure Rh(NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O crystals from Johnson Matthey. Subsequently, active catalysts were prepared from a rhodium nitrate solution which is said by Engelhard to contain excess nitric acid. It is not known why the first solution did not result in active catalysts.

The results are first summarized in table I and then given in more detail in tables II to VI and figures 1, 2 and 3.

## Discussion of results.

It may be expected that the products distribution will be affected by test conditions - temperature, pressure,  $H_2/CO$  ratio, flow rate and length of operation (aging). However, from the literature and within the range tested, these variables change selectivity only slightly. As expected lower flow rates or higher temperatures increase conversion. For comparative purposes, the results at 30 atmos., 250°C, 2  $H_2/CO$  ratio and space rate of 4000 GHSV. have been chosen as a good measure of catalyst capabilities. Table I presents an overall summary of results.

For specific comparisons, it is deemed important to make comparisons at equal conversion. Comparisons can be made by using conversion/selectivity curves, shown later.

It should be emphasized that the distribution of oxygenates is an important factor in catalyst evaluation. The relatively high C2+ oxygenates for many of the catalysts tested is noted.

### Rh- $Al_2O_3$ Table II

This catalyst typically resulted in 6% conversion of CO, with a selectivity of about 30% to oxygenates, with the balance almost all  $CH_4$ . A relatively high percentage of oxygenates is C2+, eg 75-90%. One detailed product distribution is shown in figure 1. Note the large amount of ethyl acetate.

### Rh-Alkali- $Al_2O_3$ Table III

Catalysts containing 0, 0.67, and 2.0 % Na or 1.14% K were prepared by codeposition. The effect of alkali is to lower activity considerably. The selectivity was not improved except for the 2% Na catalyst, which rose to 70%. though at low conversion (0.8-2.5%) see also fig 2. In order to be more confident that this improved selectivity is not just a low conversion phenomenon, tests will be made at lower flow rate/ higher conversion.

Also catalysts will be prepared by impregnation of  $NaNO_3$  on a Rh/ $Al_2O_3$  catalyst which has been prereduced, to find out whether the order of addition has an influence on the activity or selectivity.

### Rh-Mn- $Al_2O_3$ Table IV

Since Mn has been found to increase activity of Rh/ $SiO_2$  catalysts, addition of Mn to Rh/ $Al_2O_3$  catalysts was tried. The activity decreased and selectivity was not increased.

Rh/SiO<sub>2</sub> Table V

A Rh-Mn-Mo-SiO<sub>2</sub> catalyst was prepared similar to that described by F.G.A. Van den Berg (thesis, University of Leiden) and described in patents issued to Union Carbide. This catalyst was found to be fairly active (6% conversion) about the same as the Rh/Al<sub>2</sub>O<sub>3</sub> catalysts. The oxygenates selectivity was 50-70%. As shown in Table IV the effects of various test conditions were also explored.

## Rh/Florisil Table V

Florisil is a SiO<sub>2</sub>-MgO gel commercial product used for packing chromatographic columns. A Rh-1%Mn-1%Mo/Florisil catalyst showed remarkably high selectivity to oxygenates (80-93%) although the activity was low.

In order to follow up on this catalyst, a 3% Rh/Florisil catalyst was prepared. Very low conversion was found with high selectivity to methanol.

## Pd/ Active Carbon Table VI

It was confirmed that this catalyst from Aldrich is remarkable in producing only methanol.

## Tasks 3 and 4. Surface Structure and Surface Complexes

The infrared cell has been pressure tested successfully up to 200°C and 40 atmos. Modifications are being made which will allow us to go up to 100 atmos. At present tests on an IR cell at high temperature (250°C) are being made using Kalrez O rings. A procedure is being evolved to load, startup and shutdown the IR cell which would not put excessive mechanical and thermal strain on the window. Three out of five sections (modules) on the reactor cart have been tested. The remaining two sections are in the process of being assembled and tested.

## Other Activities.

As an educational requirement and as an aid to the project, graduate student Bhore submitted and defended before the faculty of the Department of Chemical Engineering a proposal concerning the future work to be done. Considering the rapid rate of appearance of data in recent literature, new experiments were designed in this proposal which would give rise to key results. These results will be used to discriminate between different mechanisms which are consistent with kinetic data. Some of these are temperature programmed desorption using labelled compounds and mixing of different catalysts of very small particle size.



Table II

Rh-Al<sub>2</sub>O<sub>3</sub> CATALYSTS

catalyst	p(psi)	t ° C	H /CO	GHSV	%CO Conv approx	OXYGENATES	
						%	%C2+
3%Rh/Al <sub>2</sub> O <sub>3</sub>	450	250	2	4000	6	33	ca 80
"	"	275	2	"	18	17	ca 75
"	"	"	1	2500	11	28	ca 75
"	"	"	1	"	8	28	ca 75
"	710	"	2	4000	13	22	ca 75
5%Rh high purity gamma Al <sub>2</sub> O <sub>3</sub> J.-Matthey	450	225	2	4000	2.4	37	88
"	"	250	2	"	6.2	34	90
"	"	"	2	2000	8.6	33	94
red. 300° C	750	"	2	"	13.6	33	95
"(2 hr) "	"	"	1	3000	4	48	95
reduced at 500° in H <sub>2</sub> flow for 1 hr, cooled to 150° C, kept at 450 psi and flowing H <sub>2</sub> during weekend							
"	450	250	2	4000	5	40	90
0.5%Rh/Al <sub>2</sub> O <sub>3</sub> Engelhard (1.25g)	150	250	2	1000	2.4	28	82
"	450	275	2	"	4.8	29	mostly EtOH 85
"	"	300	2	1000	13	15	84
5% Rh ex Na <sub>3</sub> RhCl <sub>6</sub> / Al <sub>2</sub> O <sub>3</sub> Tamaru catalyst	15	250	2	2000	1.2	27	82
"	200	"	2	"	0.8	19	30
"	450	"	2	"	0.9	21	30
"	"	275	2	"	1.5	17	<50

repeat of above without 1 atmos test - same results

All catalysts reduced in flowing H<sub>2</sub> at 500° C for 1 hr unless stated otherwise.

Table III

Rh- $\text{Al}_2\text{O}_3$ -ALKALI

Catalyst	p(psi)	t <sup>o</sup> C	H <sub>2</sub> /CO	GHSV	%CO Conv approx	Oxygenates %	%C2+
Rh-Na/ $\text{Al}_2\text{O}_3$ 1:1 Rh:Na 0.67% Na	450	250	2	4000	2.5	35	75
	"	275	2	"	7	25	75
	715	"	2	"	9.4	30	85
Rh-K/ $\text{Al}_2\text{O}_3$ 1:1 Rh:K 1.1% K	450	250	2	4000	2.4	32	70
	"	275	2	"	5	26	70
	750	"	2	"	5.5	27	75
Rh-Na/ $\text{Al}_2\text{O}_3$ 1:3 Rh:Na 2% Na not calcined	450	250	2	4000	0.8	70	30
	"	276	2	"	1.5	60	30
Rh-Na/ $\text{Al}_2\text{O}_3$ 1:3 Rh:Na 2% Na calcined	450	250	2	4000	1	70	35
	"	275	2	2000	2.8	53	50
	750	"	2	"	2.8	52	40

All catalysts reduced in flowing H<sub>2</sub> at 500°C for 1 hour..

Table IV

Rh- Mn/Al<sub>2</sub>O<sub>3</sub>

Catalyst	p(psi)	t°C	H <sub>2</sub> /CO	GHSV	%CO Conv approx	Oxygenates %	%C2+
3% Rh, 1% Mn on Al <sub>2</sub> O <sub>3</sub>	450	250	2	4000	3	32	85
activated by Dutch method *	750	"	2	"	3.4	32	85
	"	275	2	"	12	19	85
3% Rh, 1% Mn on Al <sub>2</sub> O <sub>3</sub>	450	250	2	"	4	30	80
calcined at 500°C	"	275	2	"	12	18	83

\* Sample air dried at room temperature is decomposed first in He flow at increasing temperatures, ending with 250°C for 1 hr., cooled to 50°C., reduced with 10% H<sub>2</sub> in He at 500°C for 1 hr., cooled to reaction temperature in He .

Table V

## Rh-Silica Catalysts

Catalysts	p(psi)	t <sub>2</sub> <sup>o</sup> C	H <sub>2</sub> /CO	GHSV	%CO Conv approx	Oxygenates %	XC2+
2.5% Rh, 0.3% Mn, 0.3% Mo/SiO <sub>2</sub> (approx Van den Berg catalyst)	450	225	2	4000	2.6	38	80
	"	"	1	2500	2.0	62	88
	"	250	1	"	5.2	60	93
	"	224	1	"	1	68	93
	"	275	1	"	12.6	45	92
	"	250	1	1250	6.7	64	94
	750	"	1	5000	2.1	72	94
	"	275	1	"	5.2	55	94
	200	"	1	2500	8.6	45	91
	"	250	1	"	2.4	53	94
	"	"	1/2	4000	0.65	61	95
	450	"	1	2500	1.8	61	93

in the conversion calculation, assumed little CO<sub>2</sub> formed  
other numbers are CO<sub>2</sub>-free calculation

2.5% Rh, 1% Mn, 1% Mo/Florisil not calcined	450	250	2	4000	1	87	35
	"	"	1	2500	1	93	36
	750	250	1	"	1	89	40
	"	275	1	"	3.5	85	33

calcined	450	250	2	4000	1.5	80	35
at 275 C, 750 psi, EtOH=MeOH							

3% Rh/Florisil calcined at 500 <sup>o</sup> C	450	250	2	4000	0.13	95	0
	"	275	2	"	0.43	80	0
only MeOH, little CH <sub>4</sub>							

Table VI

Catalyst	p(psi)	Pd-Char		GHSV	% CO Conv approx	Oxygenates	
		t°C	H <sub>2</sub> /CO			%	%C <sub>2</sub> +
5% Pd /C (Aldrich)	220	225	2	5000	1	100	0
	"	"	3	3500	2.3 only MeOH	100	0

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FIGURE I

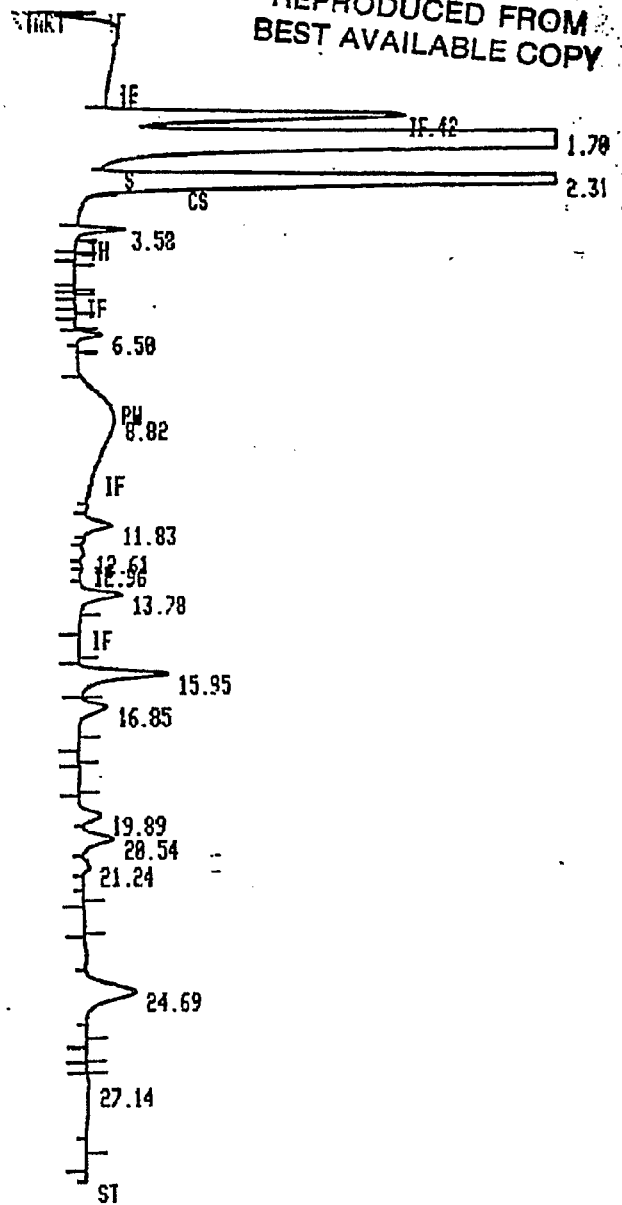
CATALYST 5% Rh- Al<sub>2</sub>O<sub>3</sub>

J.-Matthey

Pressure 750 psi  
Temperature 250°C  
G.H.S.V. 2000  
H<sub>2</sub>/CO 2

Products  
% CO converted 13.6  
% oxygenates 31  
% C<sub>2</sub>+ 92

Compound	G.C. retention time, min.	% converted to
CO	1.7	
CH <sub>4</sub>	2.31	67
CO <sub>2</sub>	3.58	
C <sub>2</sub> H <sub>4</sub>		
C <sub>2</sub> H <sub>6</sub>	6.50	2.0
C <sub>3</sub> H <sub>6</sub>		
CH <sub>3</sub> OH	11.83	1.6
CH <sub>3</sub> CHO	13.78	4.2
C <sub>2</sub> H <sub>5</sub> OH	15.95	8.0
HCOOCH <sub>2</sub> ?	16.85	1.1
i-C <sub>3</sub> H <sub>7</sub> OH	19.89	2.1
CH <sub>3</sub> COOH	20.54	2.6
C <sub>3</sub> H <sub>7</sub> OH	21.24	0.9
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	24.69	10.4

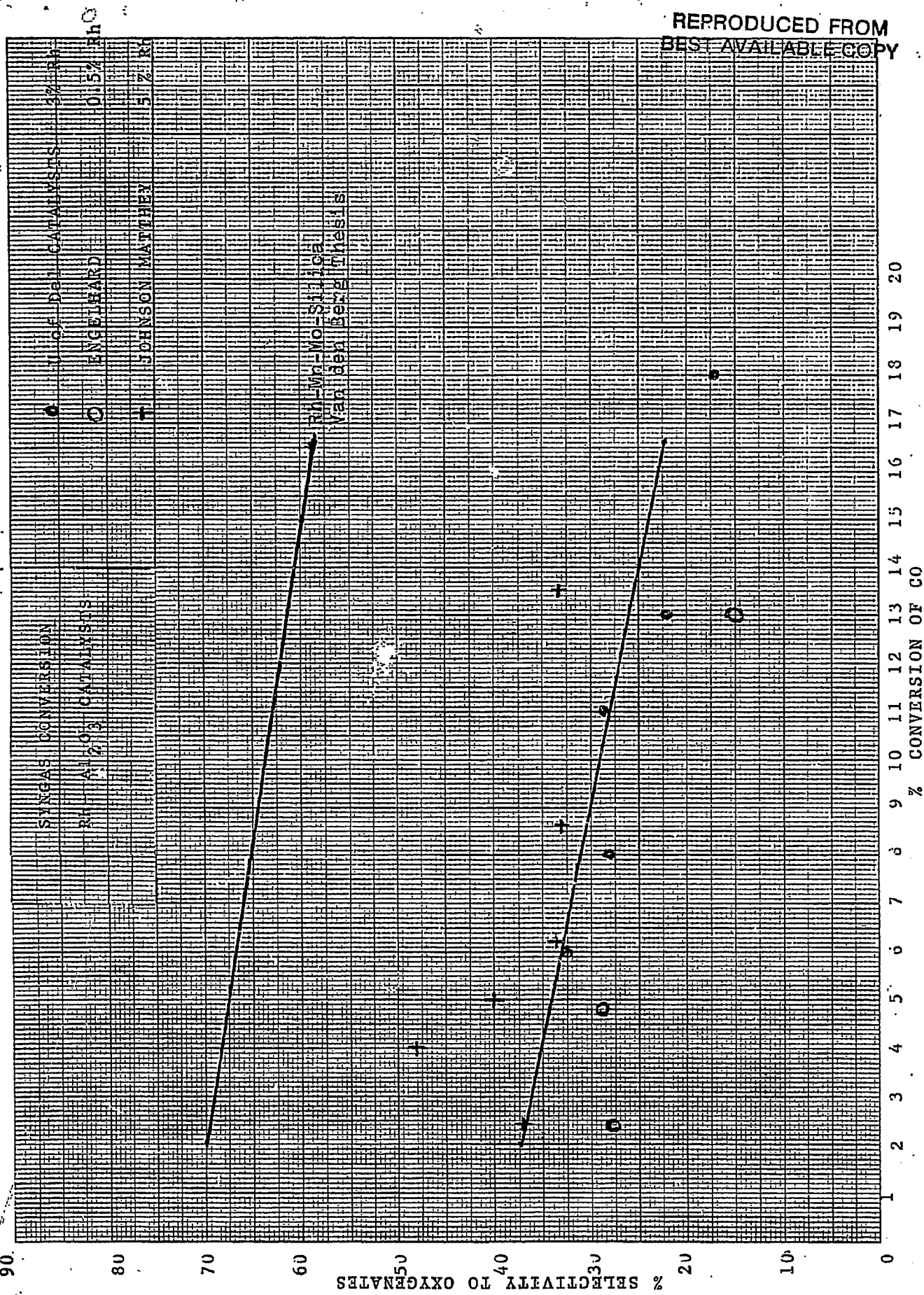


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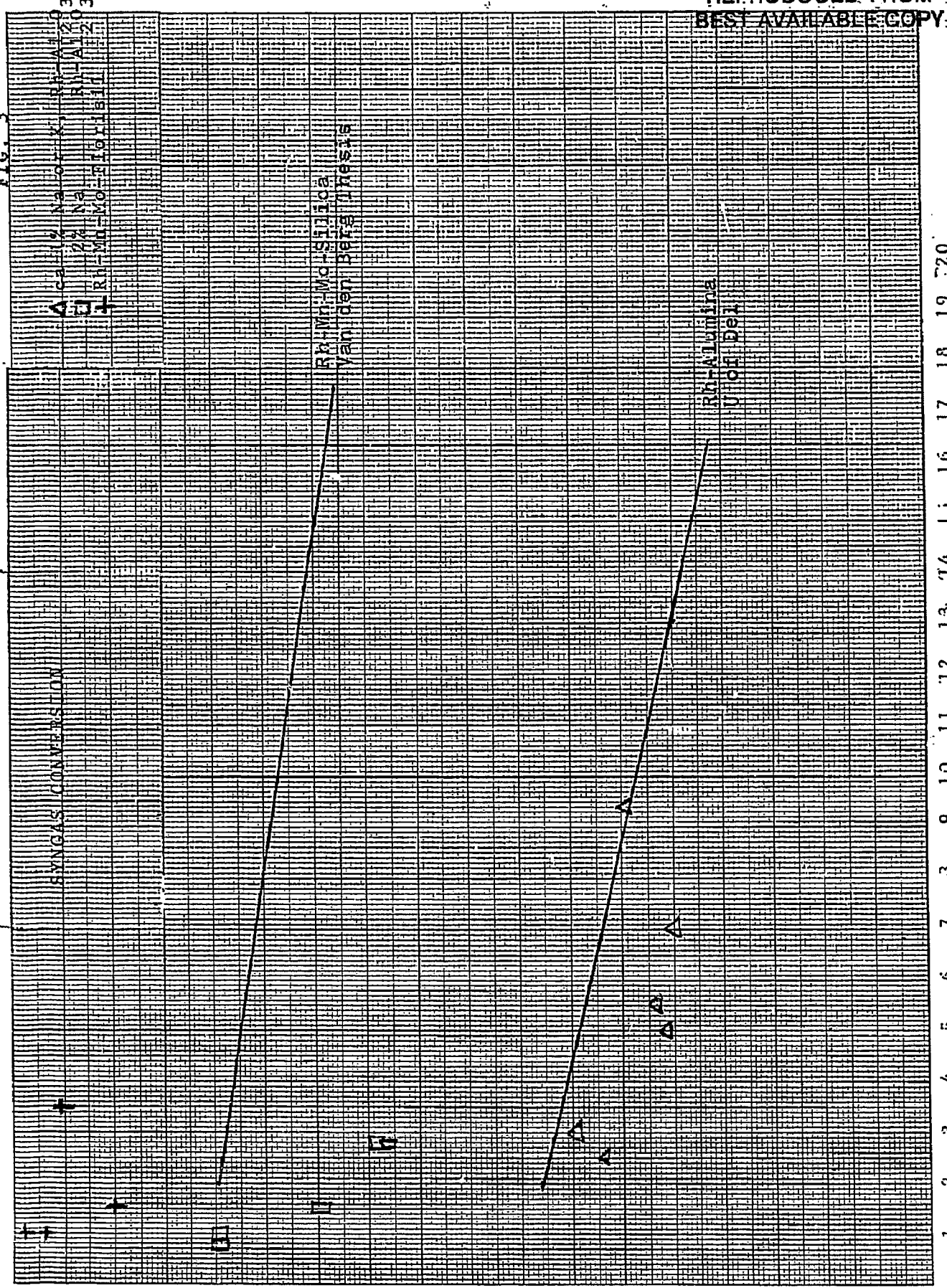
FIG. 2



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FIG. 3



DIETZEN CORPORATION  
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NO. 341-M DIETZEN GRAPH PAPER  
MILLIMETER

Acetylene, Naloxone, RA-11203  
Pt-Rh-Mo-Silica, RA-11203  
Pt-Rh-Mo-Silica, RA-11203

Pt-Rh-Mo-Silica  
Van den Berg Process

Pt-Rh-Mo-Silica  
Union Carbide



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