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TRIFUNCTIONAL CATALYSTS FOR CONVERSION TO SYNGAS TO ALCOHOLS. FOURTH QUARTERLY REPORT, JUNE 1-AUGUST 31, 1985

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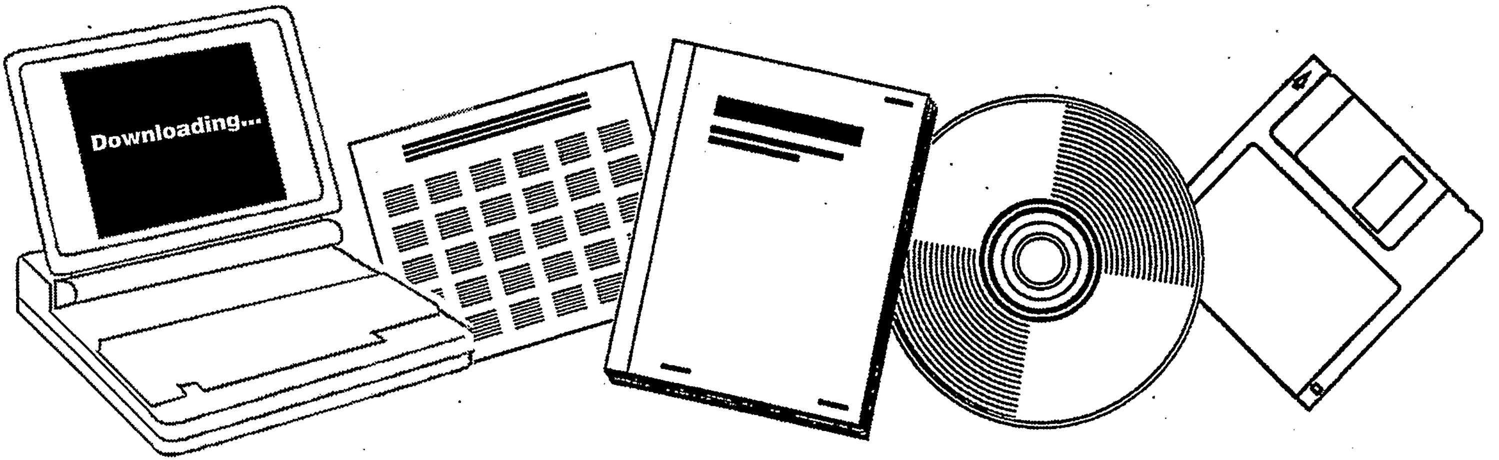

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TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

Fourth Quarterly Report for Period
June 1,1985 to August 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

A number of significant catalysts were prepared and tested for CO hydrogenation at 225° to 275° C and 450-750 psi in the flow reactor system.

Rh-Al$_2$O$_3$-Na. The dependence of selectivity on conversion level was confirmed and further clarified using catalysts of 0 and 2 % Na content. Conversion was generally varied by operating at different space rates.

Promotion of activity of Rh-Al$_2$O$_3$ was observed for addition of ions of titanium or of molybdenum, but not for manganese which decreased activity.

Rh-TiO$_2$ catalysts were found to be very active and gave relatively high selectivity to oxygenates.. The addition of lanthanum increased selectivity further.

Silica containing catalysts were prepared and tested. One, using a silicated alumina and containing Mo and Mn in addition to Rh, gave good activity and selectivity. A bimetallic Rh-Pd/silica catalyst did not perform well.

Analytical. Using the present GC system, a previously unidentified peak was found to correspond to butane in what appears to be amounts unexpectedly high (much larger than predicted by Anderson- Shultz-Flory equation). This is being further clarified.

Run data are now being computerized using Lotus 1,2,3, IBM PC. This should assist in data interpretation.

XRD is being used to check metal and support character. In one instance no rhodium metal peak was observed on freshly reduced samples but appeared after extensive catalyst use.

Infrared. The FTIR system is now operational and initial spectra are being obtained at elevated temperature and pressure.

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

Rh-Al_2O_3-Na Selectivity. See Table # 8 and 9.
To check our hypothesis (previous quarterly report) that the oxygenate selectivity is linked to the CO conversion level, selectivity being higher at lower conversion, two experiments were carried as described below.

1) 3% Rh/Al_2O_3 was tested at high flow rates, forcing low conversion.
2) 3% Rh,2%Na/Al_2O_3 tested at low flow rates, forcing high conversion.

The results from the first experiment showed that the oxygenates selectivity did not depend on conversion in the range tested (0.95-2.3%). However, the results from the second experiment showed that the selectivity decreased from 51 to 33 % when the conversion of CO increased from 0.8 to 12.6 % at 275°C,450 psi on the Na- containing catalyst. The dependence of selectivity on conversion level has not been recognized adequately in the literature.

The decrease in activity by alkali can be taken as a poisoning phenomenon. The log of activity vs alkali content is linear,Fig 1,as is often found for deactivation by poisons.

In a separate experiment ,Table # 7, to test whether the method of addition of Na would influence catalyst properties, NaOH was deposited on a prereduced Rh/ Al_2O_3 , (obtained from Johnson Matthey).The data presented shows that this catalyst behaves very similar to the co-deposit Rh-Na on Rh/Al_2O_3 .

Promotion of Activity of Rh/Al_2O_3 (Promoter Effect)

To complete our work on the Mn promoted Rh/Al_2O_3 catalysts, a 3% Rh, 3%Mn/Al_2O_3 catalyt was tested (table #1). The data showed that the activity was further reduced (compared with 1% Mn) without the selectivity being changed.

To investigate why the addition of Mn increases the activity of Rh/SiO_2 catalysts greatly, and decreases the activity of Rh/Al_2O_3catalysts, two additional promoters - Mo and Ti- were tested.These were used by previous workers, Van den Berg and Ichikawa, to promote the activity of Rh/SiO_2 .The data (table #3) shows that Mo increased the activity of Rh/Al_2O_3 greatly, surprisingly at good selectivity to oxygenates. However,the majority of the oxygenates was MeOH and DME.

In the case of Ti-promoted Rh/Al_2O_3catalysts,(table #4,5) two different reduction temperatures were used, 300° and 500° C, in view of the interesting SMSI possible in this system. The catalyst reduced at 300° was almost as active as the Rh/Al_2O_3 , with less oxygenates selectivity. The activity of this catalyst doubled when it was tested after reduction at 500° (same catalyst continued). The selectivity to oxygenates was also slightly improved.

Katzer et al found that the activity of supported Rh catalyats varied in the order

$Rh/TiO_2 > Rh/Al_2O_3 > Rh/SiO_2$

Our experiments with different promoters on Rh/Al_2O_3 show that the promoters, even though present in very small concentrations, affect the properties of the supported Rh catalysts very similar to the way the metal-support interaction affects catalyst properties. (Probably Rh/Mn oxide is slightly less active than Rh/Al_2O_3)

Silicated Alumina. (table #2)

To see whether the presence of silica in the alumina affects the cataytic properties of supported Rh, a catalyst resembling the Dutch catalyst was made with silicated gamma alumina (6% SiO_2 ,the rest Al_2O_3) with the composition 3% Rh, 0.3% Mn, 0.3%Mo/silicated gamma alumina. This catalyst gave slightly better oxygenates selectivity compared to Rh/Al_2O_3 of similar activity, but was inferior to the 3%Rh, 0.3% Mn,0.3%Mo/SiO_2 catalyst. As a consequence of the acidity of the silicated alumina support, the majority of the MeOH was converted to DME.

Rh-Titania

In view of the reported high activity of Rh/TiO_2 for CO hydrogenation, an attempt was made to see whether certain promoters can modify the selectivity of Rh/TiO_2 , producing oxygenates instead of hydrocarbons while keeping high activity.To see the influence of SMSI, all the TiO_2supported catalysts were tested after two different reduction temperatures-300° and 500° C. 3% Rh/TiO_2 was found to be extremely active (table #5) with relatively high selectivity to oxygenates, ca 25%, of which > 90% were C2+. This catalyst behaved quite similarily irrespective of reduction temperature. THe only promoter tried so far is lanthanum (from Ichikawa's work it is known that Rh/La_2O_3 has very good oxygenate selectivity). Our promoted catalyst was prepared by two methods : (a) by coating TiO_2 first with 5% La (as La_2O_3), then depositing Rh, (b) by coimpregnation of TiO_2 with Rh and La. The following conclusions can be drawn from the data (tables #5,6,7)

(a) when the catalysts were reducd at 300° C, the catalyst preparation method (sequential or co-impregnation) does not seem to have any effect. Both catalysts were as active as Rh/Al_2O_3 and have about 40% selectivity to oxygenates.

(b) promotion by La reduces the activity of Rh/TiO_2 considerably, but improves selectivity considerably.

(c) after reduction at 500° C , the two La promoted catalysts behaved differently. The coimpregnated catalyst was less active and more selective.The striking effect of reduction at 500° C was the increase in the proportion of C2+ oxygenates in the total oxygenates from 50-60% to > 90% in both cases.

These preliminary results on TiO_2 based catalysts show that the oxygenate selectivity of supported Rh catalysts can be improved, while still maintaining good activity, using proper promoters and preparation method.

Bimetallic Catalysts (table # 10,11,12,13)

Since Pd catalysts are known to be highly selective to MeOH formation from syngas under the experimental conditions being used here, an attempt was made to see whether Rh-Pd bimetallic catalysts would perform better than Rh catalysts.

In particular, Pd might decrease the formation of methane relative to methanol. A series of three catalysts were prepared using SiO_2 -57 (Davison)as support. 3%Rh,/SiO_2 ;1.5%Pd/SiO_2 ;3%Rh,1.5%Pd/SiO_2 were prepared and tested for CO hydrogenation. Rh/SiO_2 was an order of magnitude less active than Rh/Al_2O_3, but was more selective (ca 70%) to oxygenates. The 1.5% Pd/SiO_2 catalyst produced 100% MeOH without any hydrocarbons. However the bimetallic catalyst turned out to be less selective than the Rh/SiO_2 catalyst itself. XRD is being used to seek the answer to this.

A 3% Rh,1.5% Pd/Al_2O_3 catalyst was prepared and tested in a similar way. It also turned out to be less active and selective than Rh/Al_2O_3 itself.

Analytical.

One unidentified peak in our GC analysis which was thought to be an oxygenate turned out to represent butane. This peak is of considerable size in the case of Rh/Al_2O_3
(much higher than predicted by Anderson- Shultz-Flory distribution theory).The selectivities reported in quarterly report #3 will be decreased somewhat therefore.
The previous selectivities are being recalculated. Also, the reason for the unusually high butane is being sought.

Task 3 and 4. Surface Structures and Surface Complexes.

XRD

Powder x-ray diffractograms are being taken for all the used and some of the freshly reduced catalysts. In most cases the Rh metal peak could not be observed, indicating that the Rh particle size is smaller than the detection limit by the XRD being used (30-40 Å). Several interesting observations have come out of the XRD work so far.

(a) The inactive Rh/Al_2O_3 catalysts prepared using the Rh nitrate crystals from Johnson-Matthey, gave a distinct Rh metal peak in the XRD,Fig. 2. The Rh particle size calculated from line broadening is about 100 Å . The present belief is that the inactivity of that catalyst is due to poisoning by sulfate in the nitrate and not due to large Rh crystal size.

(b) 5% Rh/gamma-Al_2O_3 ,reducced catalyst obtained from Jo hnson-Matthey, as received, turned out to be on Boehmite and not on gamma alumina as believed. No Rh peak was detected indicating either small particle size or incomplete reduction.

(c) 3%Rh,2%Na/Al_2O_3 . This catalyst when reduced at 500°C and used in the reactor for about two days did not show any Rh peak after such use. However, when the used catalyst was exposed to air, rereduced at 500°C and reused in the reactor for about a week,at high conversion (up to 12%),
a Rh peak was then observed, again indicating 100 Å size

Infrared Measurements.

The high-pressure cell system (the cart) was tested completely and at present it can hold 300 psig and go to 250 C. The cell at present can withstand pressures up to about 500-600 psig. However, a defective high temperature gas sampling valve needs to be replaced or repaired to extend the range. Modifications have been made to decrease the start-up time. These include :

(1) change in the support system for the cell so that the cart can be rolled into FTIR instrument.

(2) by rearranging the controls of massflow controller for easy access.

Because of temperature limitations insitu reduction above 250°C is not now possible. To go to a higher temperature we are anticipating using Grafoilseals instead of Kalrez.

Chemisorption

To normalize the kinetic data in a scientific way, the chemisorption apparatus has been set up on Micromerinco 2100.The required purification system has been set up. A standard catalyst ASTM 3908 (0.5% Pt/Al_2O_3) has been tested and the results obtained agree with those reported from other laboratories.

Kinetic Analysis

To analyse the kinetic data we are using Lotus 1-2-3 program on IBM PC which has built-in spreadsheet/graphics manipulation capabilities.This is expected to assist in analysis of the results as additional data are developed.

The ability to perform analyses using our single column GC has many advantages. However, in a few instances the observed peaks do not adequately resolve the product compounds.

At present, our GC system does not separate MeOH and propane. However this is being handled in the following way.Propane is being predicted by using a calculation employing the A-S-F relationship.(methane and ethane as measured are used as the basis for calculation) and then MeOH is calculated to correspond together with propane to the peak area.

(corrected for butane &
methanol-propane)

CATALYST	P(PSI)	T°C	H_2/CO	GHSV	%CO CONV	% OXYEN.	%C2+
#1) 3%Rh-3%Mn/γ-Al_2O_3	450	250	2	3000	4.1	20.3	>80
calcined in air at 500° C	450	250	2	1500	6.8	27.5	87
and reduced at 500° C	after overnight						
	450	250	2	1500	4.6	29	92
	450	265	2	3000	5	22.6	90
	750	250	2	1500	5.7	31	89
	750	275	2	1500	18.7	21.7	94
		very little CO_2					
#2)	450	225	2 .	3000	2	ca 34	ca 60
3%Rh, 0.3%Mn, 0.3%Mo/	lots of DME. Then overnight						
silicated γ Al_2O_3	450	250	2	1500	9.4	34	52
He 160°,250° H_2 300°, 500° C	750	250	2	1500	15.3	40	36
	moderate CO_2						
#3)	450	225	2	3000	9.7	40	ca 25
3%Rh,2.8%Mo/γAl_2O_3	450	230	2	3000	12.7	38	ca 25
(Rh/Mo atom =1)	750	225	2	3000	15	45	ca 25
calcined in air 500° C	CO_2 high, DME high						
reduced at 500° C							
#4)							
3%Rh,1.46%Ti/γ-Al_2O_3	450	250	2	ca 3600	4.8	16	>85
(Ti/Rh atom =1)	450	275	2	3600	16.3	11	>90
calcined at 500° C	750	275	2	3600	18	13	>90
reduced at 300° C							
then reduced at 500° C	450	250	2	3600	8.8	20	>90
	750	250	2	3600	9.2	25	>90
#5)							
3% Rh,/TiO_2	450	225	2	ca 2500	9.0	26.7	>90
calcined in air at 500° C	450	235	2	ca 5000	7.7	24.5	>90
educed at 300° C	750	235	2	5000	9.4	25.2	>90
	750	225	2	2500	12.4	28.6	>90
	little CO_2 ,no DME						
reduced at 500° C	450	235	2	5000	8.2	24	>90
	450	225	2	2500	10.6	27.7	>90
	750	225	2	2500	11.7	29.2	>95
#6)							
3% Rh/5%La-TiO_2	450	225	2	ca 4000	1.6	57	37*
La first, Rh later	450	250	2	4000	4.6	39	50^
calcined in air 500° C	450	250	2	ca 2000	5.9	37	65
reduced at 300° C	750	250	2	2000	6.7	43	67
	750	250	1	ca 3000	2.5	48	68
* only MeOH+EtOH,trace ethane,little CO_2, ^ no acetaldehyde,							
Then reduced at 500° C	450	250	2	ca 2000	11.4	31	95
	750	250	2	2000	9.2	38	92

CATALYST	P(PSI)	T°C	H_2/CO	GHSV	%CO CONV	% OXYGEN	%C2+
#7)							
3 %RH,5%La/TiO$_2$	450	250	2	2000	5.3	39	74
co-impregnation	750	250	2	2000	5.9	37	64
calcined at 500° C		then reduced at 500 C					
reduced at 300° C	450	250	2	2000	5.2	38	91
	450	275	2	2000	17.9	22	91
rereduced at 500° C	750	275	2	2000	16.9	23	91
	750	250	2	2000	6.2	48	89
#(8) experiments to find the relationship between conversion and selectivity							
3% Rh/γ-Al$_2$O$_3$	450	250	2	9000	2.3	25	ca 90
calcined in air at 500° C	450	250	2	13500	1.5	26.4	ca 90
reduced at 500° C	450	250	2	18000	0.95	25.3	ca 90
#9)	450	275	2	375	12.6	32.9	>90
3% Rh,2% Na/ -Al$_2$O$_3$	450	275	2	750	6.0	38.1	93
calcined in air 500° C	450	275	2	1500	3.1	45.6	91
reduced at 500° C	450	275	2	2250	1.7	42.7	90
used in the reactor	450	275	2	3000	1,5	45.1	90
before red. again 500° C	450	275	2	3600	0.8	51	>90
#10) Silica-supported and bimetallic catalysts							
3% Rh/SiO$_2$ (57)	450	275	2	1500	2.9	63	97
calcined in air at 500° C	450	250	2	1500	0.6	74.4	97
reduced at 500° C	750	275	2	1500	3.0	68	94
	750	275	1	1500	1.4	76	96
very little CO$_2$,ethane.							
#11)							
3% Pd/SiO (57)	450	250	2	3000	0.17	100	0
calcined in air at 500° C	450	250	2	1500	0.43	100	0
reduced at 500° C.	750	250	2	1500	0.51	100	0
	750	275	2	1500	1.2	100	0
little CO$_2$, trace of DME peak							
#12)							
3% Rh,1.5% Pd/SiO$_2$ (57)	450	250	2	3000	3.9	28	100*
sequential impregnation,	450	275	2	1500	2.0	50	90^
Rh first, calcined in He							
at 300 C ,reduced at 500° C							
* acetaldehyde- only product detected. ^ MeOH,acetaldehyde, EtOH,MeOAc,EtOAc detected							
#13)							
3% Rh,1.5% Pd/γ-Al$_2$O$_3$	450	250	2	1500	6.1	19	92*
same treatment as	450	275	2	3000	9.5	13	85
above catalyst	750	275	2	3000	12.8	14.4	88
	750	250	2	3000	4.2	20	90
	450	250	2	1500	5.0	15	>90
* typical Rh/Al$_2$O$_3$ products, very little CO$_2$.							

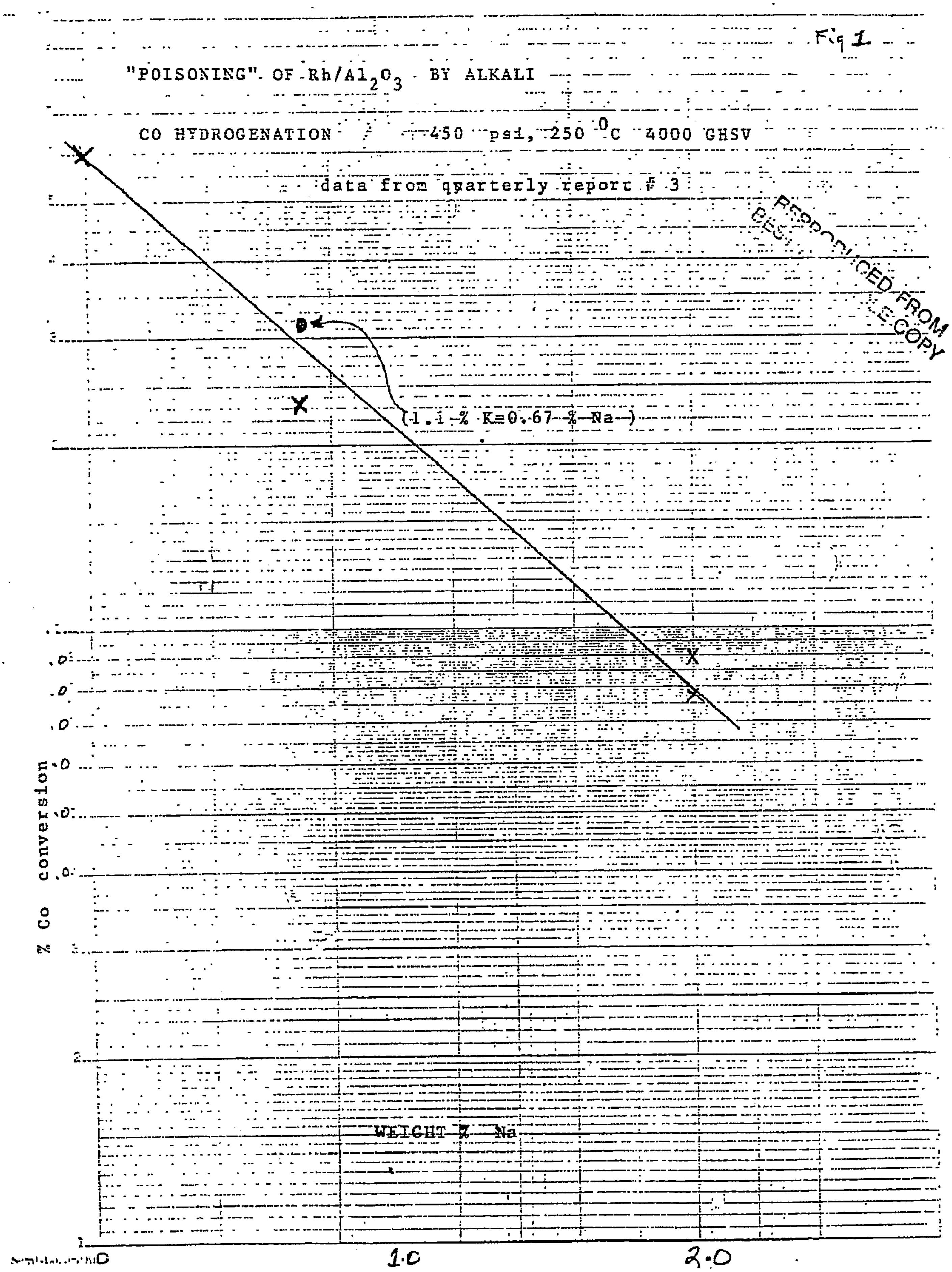
CATALYST	P(PSI)	T °C	H_2/CO	GHSV	%CO CONV	% OXYGEN	%C2+
#14) 5% Rh/γ-Al_2O_3 (Johnson Matthey) said to be reduced, deposited thereon 1 % Na from NaOH, red. 500°C	450	250	2	1500	4.9	53	76
	450	275	2	1500	7.8	33	90
	450	275	2	1500	7.1	36	88
	750	275	2	1500	9.1	42.6	83
	750	250	2	1500	2.7	65	77

Fig 1

"POISONING" OF Rh/Al_2O_3 BY ALKALI

CO HYDROGENATION 450 psi, 250 °C 4000 GHSV

data from quarterly report # 3



RH3%/AL203 ;USED CATALYST ;BAD ONE
CHAKKA SUDHAKAR 8/29/85
NO INTERNAL STANDARD
MAX COUNT = 4910

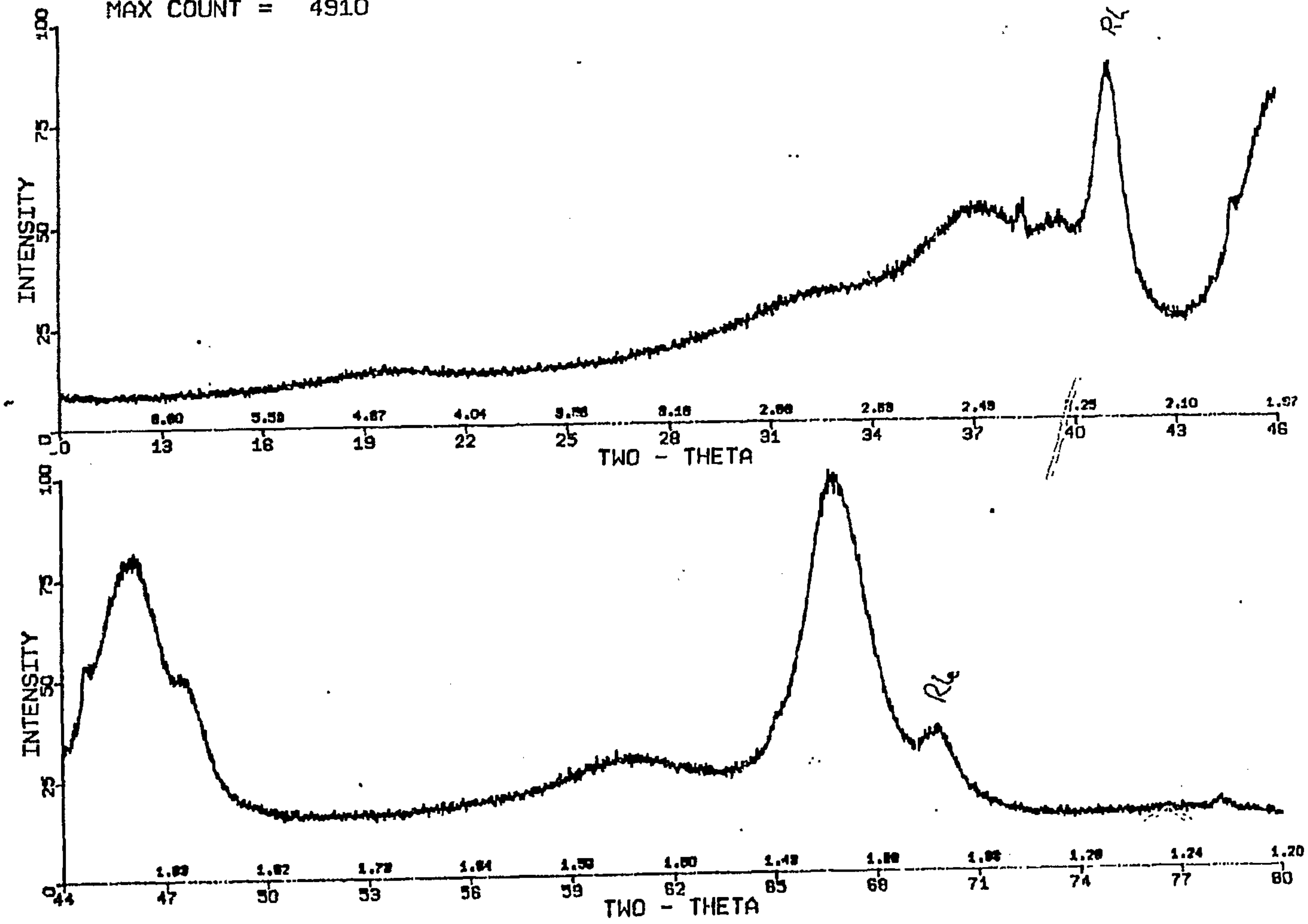


Fig 2