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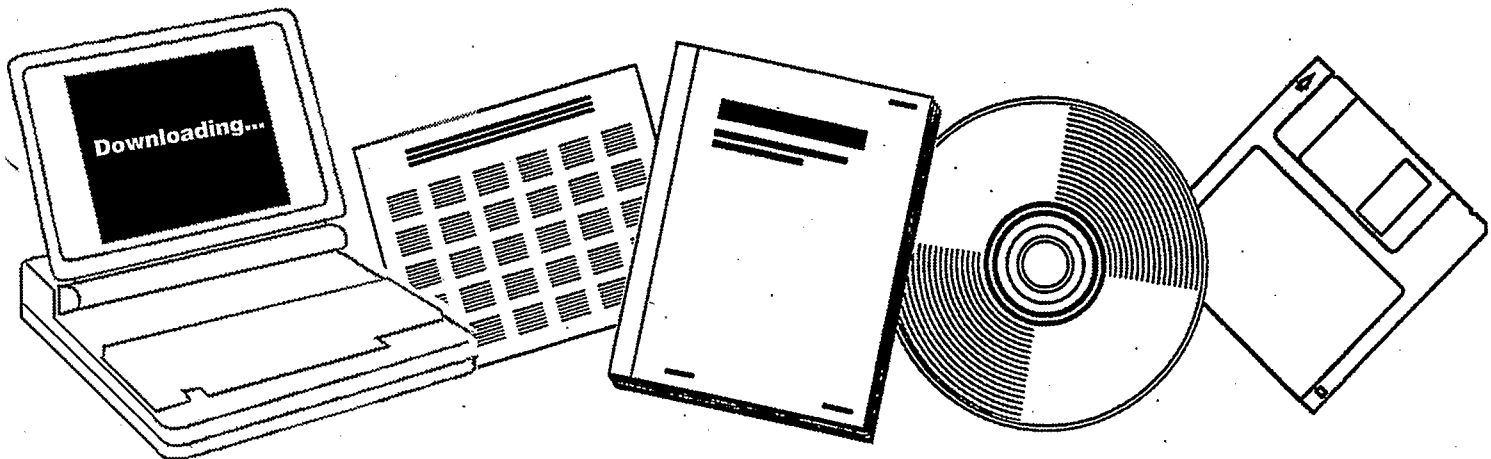
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**TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF
SYNGAS TO ALCOHOLS. SEVENTH QUARTERLY
REPORT, MARCH 1-MAY 31, 1986**

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

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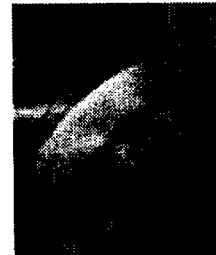
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TRIFUNCTIONAL CATALYSTS
FOR CONVERSION OF SYNGAS TO ALCOHOLS

Seventh Quarterly Report for Period
March 1 to May 31, 1986

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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

TRIFUNCTIONAL CATALYSTS
FOR CONVERSION OF SYNGAS TO ALCOHOLS

ABSTRACT

Emphasis was placed on structure characterization of catalysts previously prepared and tested for activity and selectivity for hydrogenation of CO. Two series of Rh/Al₂O₃ catalysts were examined - those modified by addition of Na or by addition of Mo.

Examination of Rh/Na/Al₂O₃ catalysts by transmission electron microscopy confirms the size of Rh particles, about 70 Angstrom units, and EDAX measurements, the presence of Al, Rh and Na when applicable.

Infrared measurements of CO chemisorbed on Rh/Al₂O₃ show linear and bridged complexes. With addition of Na, the C - O stretching frequency decreases, implying a stronger C - Rh bonding. The implications of this on the catalytic activity and selectivity are discussed.

Temperature programmed reduction (TPR) measurements show broad peaks consistent with well-dispersed Rh. The amount of hydrogen uptake indicates the reduction of Rh from 3+ TO 0, within the accuracy of the test. Further work will be reported later.

In regard to Rh/Mo/Al₂O₃ catalysts, a more detailed examination of the products distribution shows that the percentage C₂ oxygenates stays the same as for Rh/Al₂O₃, even though the activity of the catalyst has increased ten fold. The C₁ oxygenates have been greatly increased, at the expense of decreased CH₄. This implies that CH₄ and CH₃OH come from the same intermediate.

The energy of activation was estimated to be 22,000 cal per mole for both Rh/Al₂O₃ and Rh/Mo/Al₂O₃. This leads to the important conclusion that the increased activity of Mo modified catalysts is not due to a lowering of the activation energy but to more efficient site utilization, possibly by more effective activation of hydrogen by Mo.

TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

INTRODUCTION

Previously, emphasis was placed on the preparation of chemically modified Rh/Al₂O₃ catalysts and testing them for activity and selectivity for syngas conversion. Now, emphasis has been placed on characterization of these catalysts, especially two series, namely those modified by addition of Na or by Mo.

This is a progress report. Some results provide important conclusions, while other lines of investigation require more data to draw firm conclusions.

INFRARED MEASUREMENTS

The infrared spectra of CO on Rh/Al₂O₃ and on Rh/Na/Al₂O₃ are illustrated in Fig. 1. Both bridged and linear species are identified through reference spectra established by Yates and others, Fig. 2. Significantly, the C-O stretching frequency is shifted to lower values for catalysts containing Na. This indicates a weaker C-O bonding and implies a stronger C-Rh bonding. The Na-containing catalysts are much less active than unmodified Rh/Al₂O₃ catalysts. There are different possible explanations. (a) Due to increased back-donation of electrons into the antibonding orbitals of the adsorbed CO molecule, stronger Rh-CO bonding and weaker C-O bonding results. As a consequence, dissociation of CO becomes more facile, leaving more C on the alkali doped catalysts compared to undoped catalysts.

This C results in lower catalytic activity. (b) Na blocks the Rh ensemble sites that dissociatively chemisorb CO (one Na atom/ion can effect 25 Rh atoms according to Wayne Goodman.) The catalytic activity decreases as a result. Since methanol formation does not require the CO dissociation step, its formation is not affected by Na doping. (c) An alternative explanation is that the tighter bonding of the CO precludes H₂ from being activated and hence decreases the hydrogenation reaction rate. It is known for Rh/SiO₂ catalysts that CO inhibits the reaction rate, the rate is equal to $A \exp(-24,000/RT) P_{H_2}^{.04} P_{CO}^{-.55}$ [M.A. Vannice, J.Catal. 37, p449,462 (1975)].

ELECTRON MICROSCOPY - EDAX

The texture of a Rh/Al₂O₃ catalyst (used) is shown in the transmission electron micrograph, reproduced as Fig. 3. Several dark particles can be seen of a size, about 70 Ångstrom units, consistent with a rhodium crystallite size deduced from CO chemisorption measurements reported previously. X-ray diffraction patterns confirm small crystallite size.

An EDAX examination of this same sample is shown in Fig. 4. As expected, the elemental analysis provided shows major Al, a lesser Rh peak and little or no Na.

Similar electron microscope studies for Rh/Na/Al₂O₃ catalysts are underway. More data is needed to interpret preliminary results obtained.

TEMPERATURE PROGRAMMED REDUCTION /DESORPTION (TPR/TPD)

The TPR/TPD data was provided by S.B.Ziemecki of the DuPont Company without charge, as arranged by W.H.Manogue. These experiments were carried out as a feasibility study for future experiments to be carried out at the University of Delaware.

The objective is to determine if heating at a linear rate in 5% H₂ in N₂ while monitoring hydrogen uptake by thermal conductivity can distinguish between 3%Rh/Al₂O₃ catalysts containing Na in atom ratios of Na/Rh of 0, 1 and 3.

The TPR procedure involves heating a sample at a linear rate in flowing gas with the inlet and outlet gas composition compared in two sides of a thermal conductivity detector. The outlet gas is dried in a dry ice/acetone cold trap before analysis. The difference signal from the detector is stored on a time-sharing computer as a function of time at a sampling rate of 10 points per second. The output of the furnace thermocouple is similarly recorded to insure that a linear heating rate is maintained. The combined output has a resolution of 3 points per second. Hydrogen consumption is quantitated by calibration from the area, in millivolt minutes, under the time trace of the thermal conductivity detector output. For convenience in interpreting the data, time has been replaced by temperature in the graphs of the results.

A sample of 75 mg of catalyst (22 micromoles of Rh) was heated at 40 deg C/min in 60 cc/min of 5% H₂ in N₂ from room temperature to about 660° C. The sample was cooled down within 5 minutes to about -40° C in the same stream. The

flow was switched to pure nitrogen at the same flow rate for temperature programmed desorption which was carried out at the same heating rate. This rate was chosen for convenience after earlier studies in this equipment with Pd/Al₂O₃ had shown only minor changes from varying the heating rate from 5 to 50 deg C /min. The peak area which represents hydrogen uptake were accurate to 5-7%. At higher rates the peaks were sharper and the maximum temperature was slightly shifted.

For oxidation runs the catalyst after TPD was cooled to room temperature in N₂ stream and the flow switched to 60 cc/min of 2% O₂ in He.

Results

The reproducibility of TPR is quite good as is shown in Fig. 5 for two runs with fresh 3%Rh/0.67%Na/Al₂O₃ samples. Fig. 6 shows significant differences between catalysts. The 3% Rh,0.67%Na/Al₂O₃ catalyst whose TPD was different from that of other catalysts was made from a 'bad' Rh supply (thought to be contaminated with sulfur). Rhodium seems to be well dispersed in all cases as manifested by the broad appearance of the TPR profiles. Hydrogen consumption for the Na- free catalyst is 31 mv-min corresponding to 3H/Rh. A repeat run (not shown) with this material gave 32. The data suggest the rhodium is present as Rh₂O₃ before reduction.

A number of additional samples have been tested and the data are being analysed.

Rh/Mo/Al₂O₃ CATALYSTS - PRODUCTS DISTRIBUTION

The products distribution obtained with Rh/Mo/Al₂O₃ catalysts was presented in the last quarterly report. A more detailed examination reveals further insight into the reaction mechanism as influenced by the Mo. Table I presents the results of such calculations, (CO₂-free basis). As shown in the table with increasing Mo concentration (a) the total oxygenates formed increased (b) % C₂+ oxygenates decreased (c) CH₄ formation decreased and (d) the activity of the catalyst increased significantly. Closer observation of the oxygenates products distribution shows that the % C₂ oxygenates formation stayed remarkably constant, even though the activity of the catalyst increased more than 10 times on Mo addition. The right hand column of this table is the total C₁ product, ie C₁ oxygenates plus C₁ hydrocarbons formed. The % total is almost constant, even though the total activity changes by an order of magnitude. These data are consistent with the hypothesis that both CH₃OH and CH₄ are formed from the same intermediate. The greatly increased C₁ oxygenates for Mo containing catalysts can be as due to the decrease in formation of CH₄ from this intermediate, with formation of C₂ oxygenates remaining constant.

Rh/Mo/Al₂O₃ CATALYSTS - KINETICS

The kinetic expression for CO hydrogenation to all products over Rh catalysts supported on SiO₂ has been formulated as

rate = exp (-24,000/RT) $P_{H_2}^{.64} P_{CO}^{-.33}$. This is consistent with high coverage of the Rh by CO.

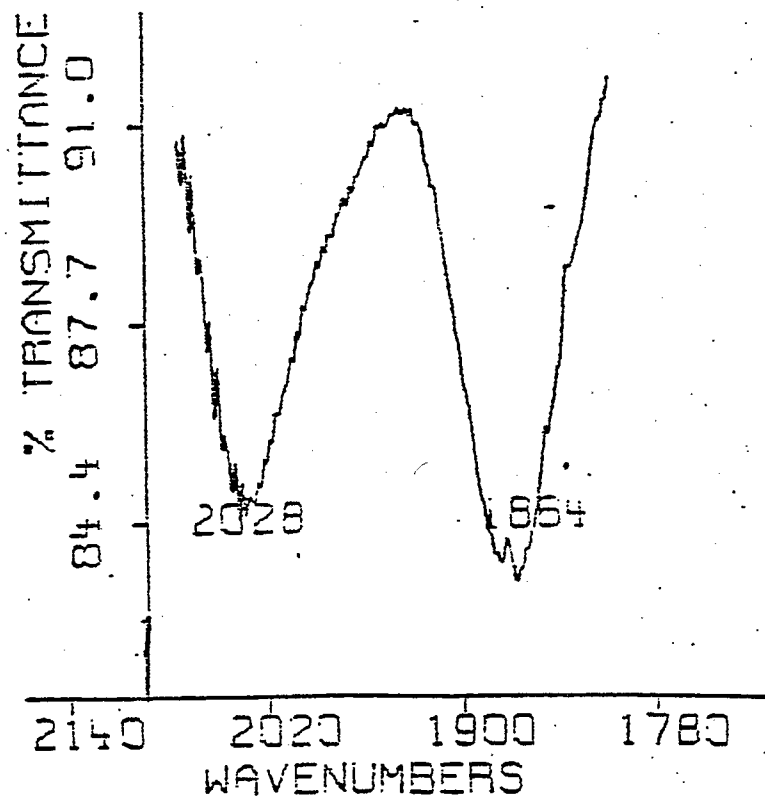
In the present research, E_{act} for both Rh/Al₂O₃ and Rh/Mo/Al₂O₃ was found to be about 22 Kcal per mole, Fig 7. A slightly lower value (17,000) has also been reported, for Rh/Mo/Al₂O₃ catalysts which were an order of magnitude less active. (H.C.Foley, 'Bimetallic Catalysts Comprised of Dissimilar Metals for Reduction of CO with H₂'. Seminar, U. of Delaware, March 1986). It is significant that the value of the activation energy is not lowered by the addition of Mo. Therefore, the important deduction is that the major increase in activity engendered by Mo is due to increased effective site availability.

Thus, if the concentration of surface hydrogen atoms is limiting because of strong chemisorption of CO, then an increase in the available H by Mo would enhance the rate of reaction. This might occur by a 'weakening' of CO chemisorption on the Rh, or what seems more likely, by the activation of H₂ on the MoO₃ adjacent to Rh with a sort of 'reverse spillover' to the Rh active site where CO is chemisorbed. Thus the ensemble would be a dual metal-metal oxide ensemble (Rh-MoO₃). Also, the effect of Rh may be to assist partial reduction of MoO₃, thereby imparting

increased activity. The great increase in oxygenates selectivity can be explained by the rapid hydrogenation of the oxygenate surface intermediate which is common for formation of both methane and methanol. These considerations can lead to experiments to determine the alternative possibilities.

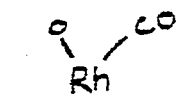
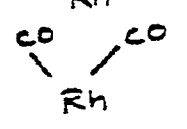
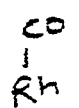
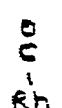
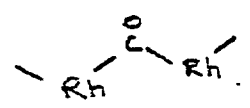
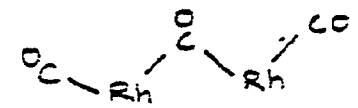
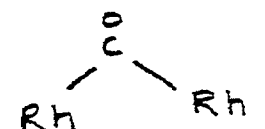
INFRARED SPECTRA OF 3%RH/ALUMINA
AT 200C AND 1 ATM

FIG. 1



| | wavenumbers(cm ⁻¹) | |
|------------------------------------|--------------------------------|------------|
| | linear CO | bridged CO |
| 3%Rh/Alumina (200C,1 atm) | 2028 | 1864 |
| 3%Rh 2%Na /Alumina (200C,10atm) | 1987 | 1844 |

PROPOSED CO SPECIES ON Rh/Al₂O₃ and THEIR FREQUENCIES.
(Yates et al)

| FREQUENCY RANGE ^a | VARIATION WITH COVERAGE | SITE DISTRIBUTION ^b | OXIDATION STATE | PROPOSED STRUCTURE |
|------------------------------|-------------------------|--------------------------------|-----------------|---|
| 2136 | No | A | III | RhCl ₃ (CO).2H ₂ O |
| 2116-2120 | No | A | II |  |
| 2096-2102 2022-2032 | No | A | I |  |
| 2082-2100 | ? | ? | I |  |
| 2042-2076 | Yes | C | 0 |  |
| 2090-2020 | ? | C | I |  |
| 1900-1920 | Yes | C | 0 |  |
| 1845-1875 | Yes | C | 0 |  |

a - cm⁻¹

b- A=Atomic
C=Cluster

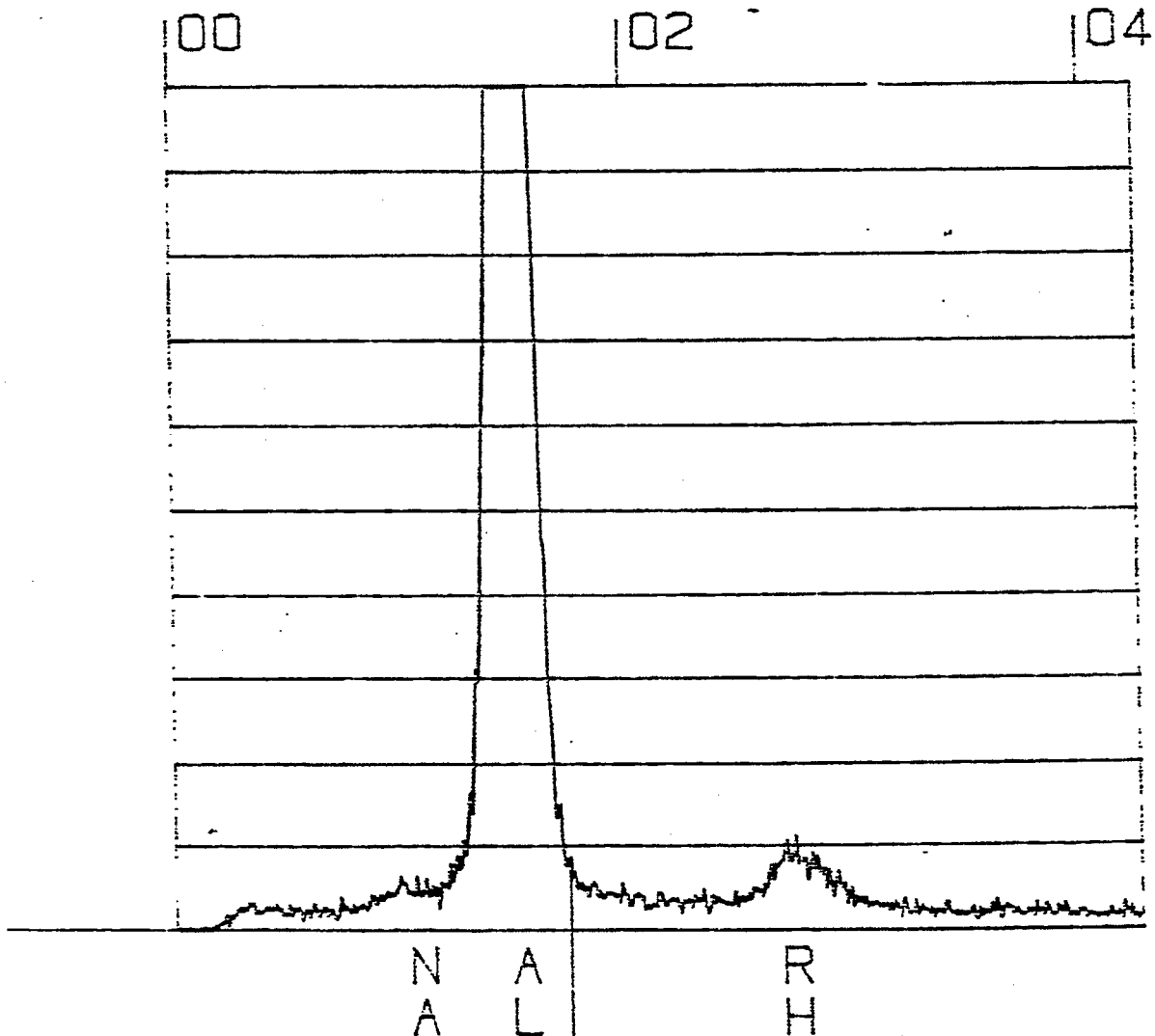


FIG. 3 TRANSMISSION ELECTRON MICROGRAPH

3 % Rhodium on gamma Alumina

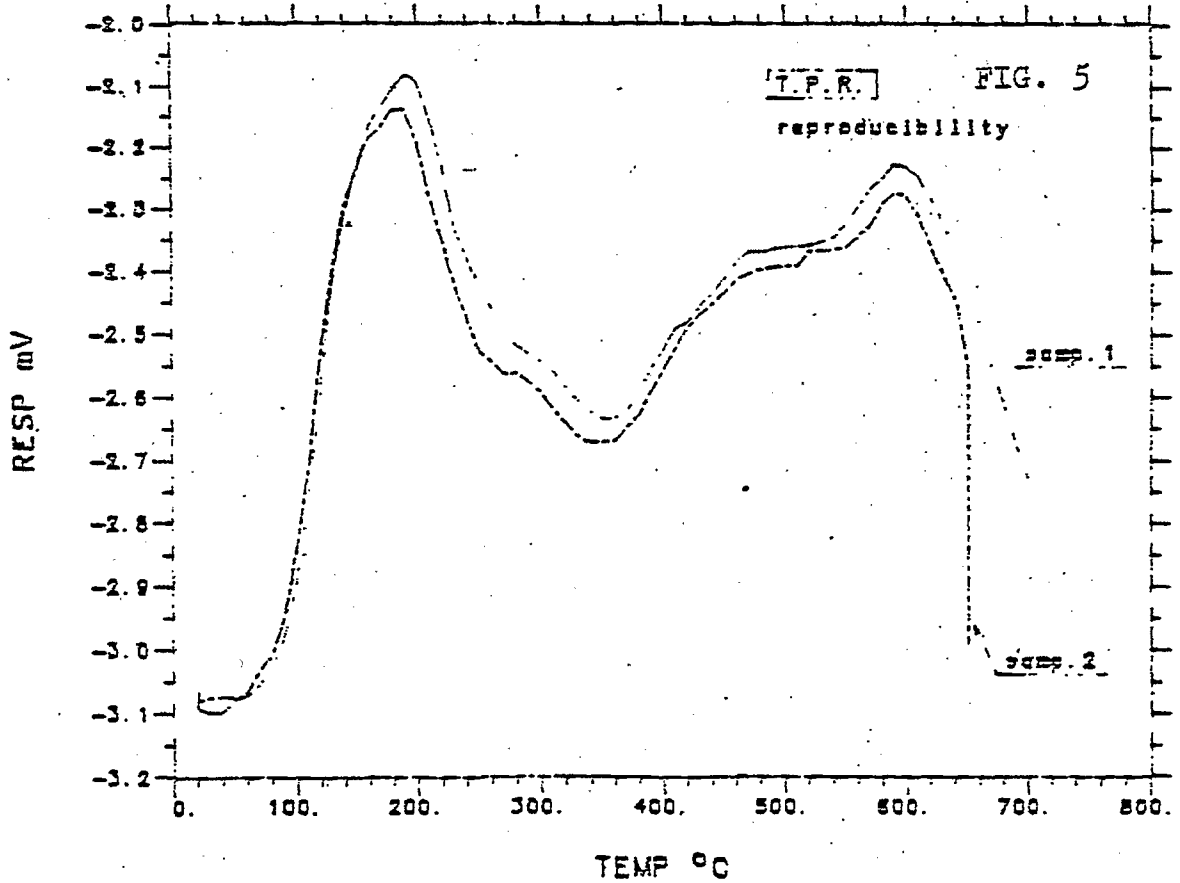
3.2 mm = 100 Å

03-APR-86 09:39:12
RATE: CPS TIME 100LSEC
00-20KEV: 10EV/CH PRST: 100LSEC
A: RH/AL203 USED B:
FS= 788 MEM: A FS= 100

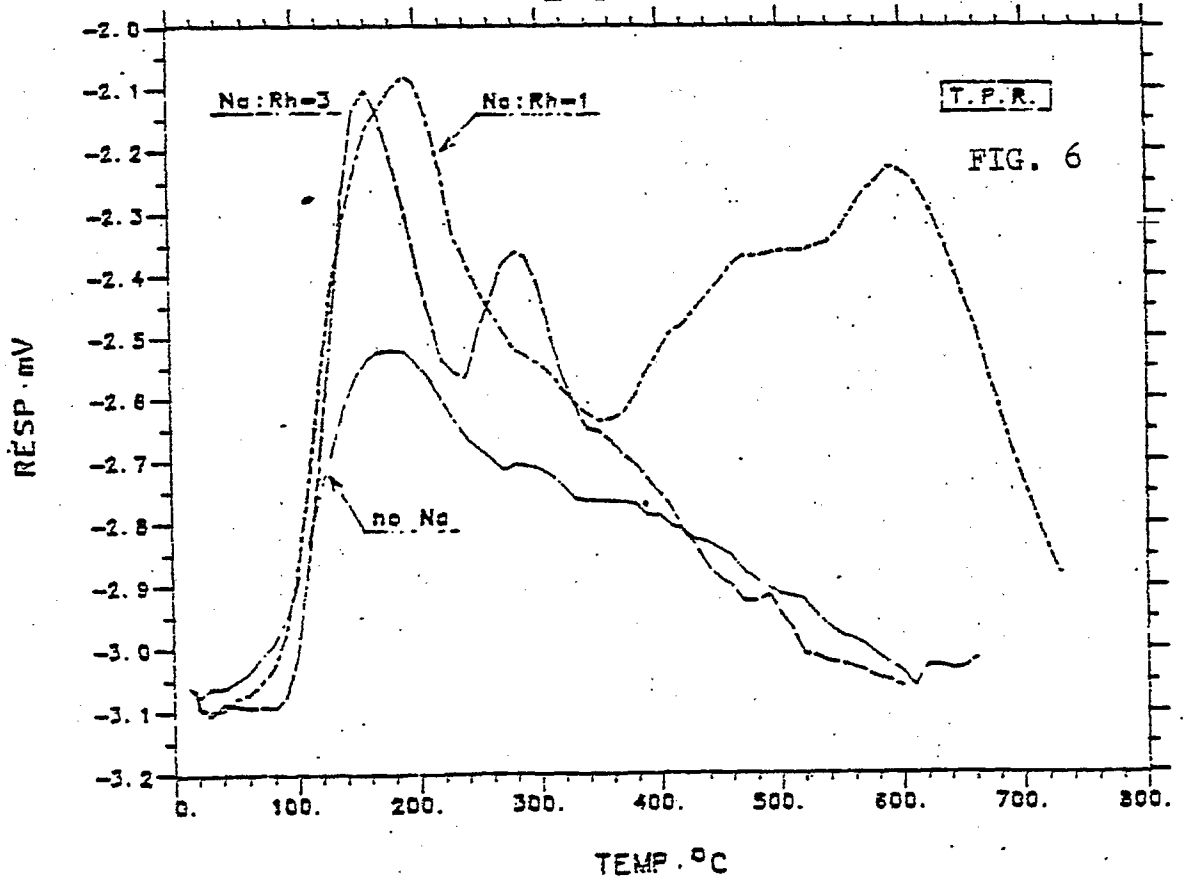


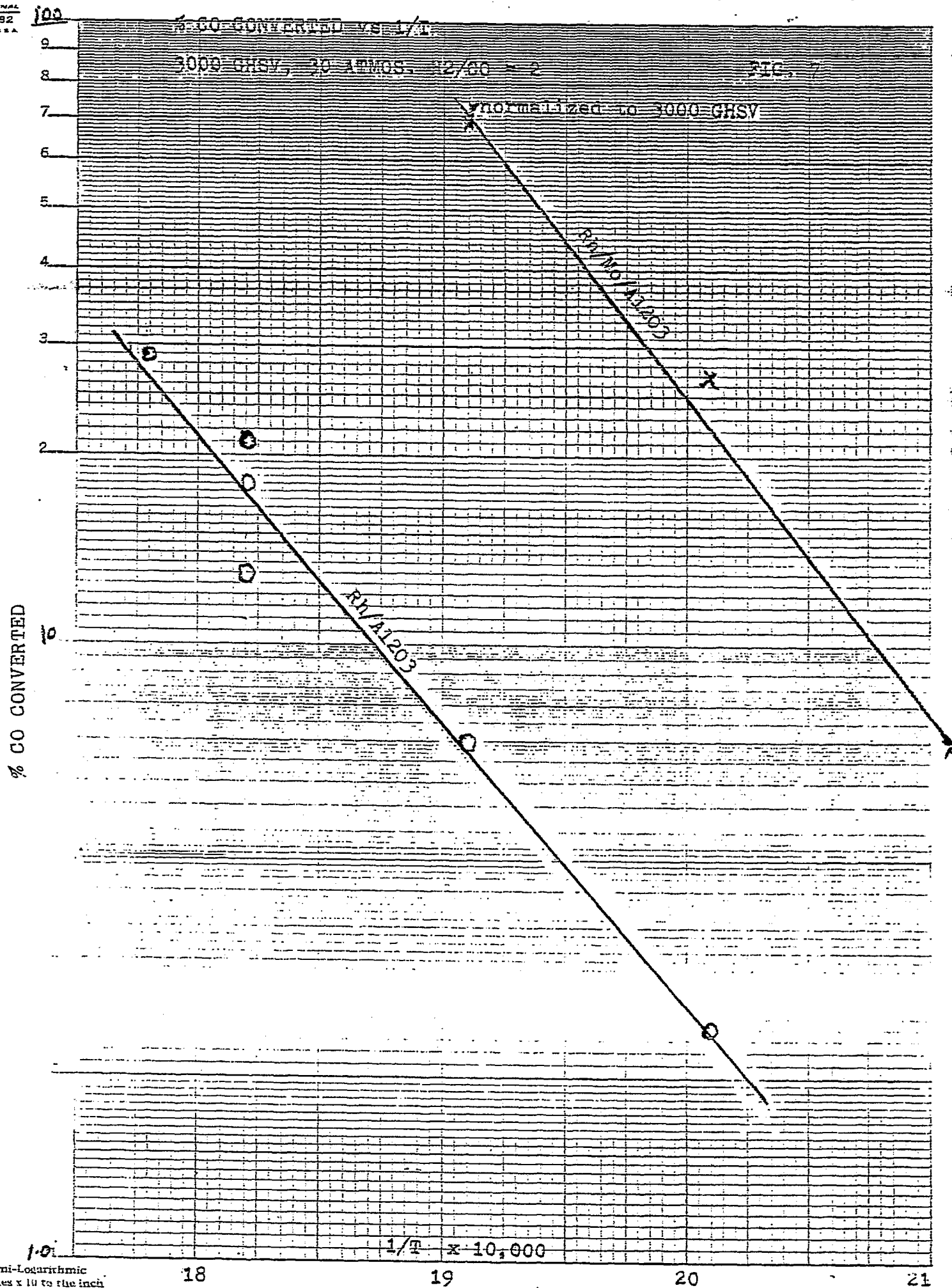
CURSOR (KEV) = 01.740 EDAX

3%Rh, 0.67%Na/Al₂O₃



3% Rh/Al₂O₃ from U. of D.





Semi-Logarithmic
24 cycles x 10 to the inch

Table I : Effect of Mo on the product distribution in CO hydrogenation over Rh/Mo/Al2O3 catalysts at 30 atmos., H₂/CO = 2

| Catalyst | Temp.°C | GHSV | % CO Conv. | % Total Oxygen. | %C ₂ + Oxygen. | %CO to CH ₄ | Oxygenates distribution | | | CH ₄ + C ₁ Oxyg |
|--|---------|-------|------------|-----------------|---------------------------|------------------------|-------------------------|----|-----|---------------------------------------|
| | | | | | | | C1 | C2 | C3 | |
| Rh/Al ₂ O ₃ | 250 | 3000 | 5.7 | 30 | 82 | 60 | 5 | 21 | 3 | 65 |
| Rh, 2.8% Mo/Al ₂ O ₃ | 225 | 3000 | 9.0 | 59 | 42 | 35 | 34 | 22 | 2.4 | 67 |
| Rh/7.5% Mo/Al ₂ O ₃ | 250 | 36000 | 5.3 | 65 | 27 | 27 | 47 | 17 | 0.7 | 74 |
| | 235 | 18000 | 6.0 | 69 | 28 | 24 | 50 | 17 | 2 | 74 |
| | 200 | 3000 | 7.3 | 86 | 17 | 9 | 71 | 13 | 2 | 80 |

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