



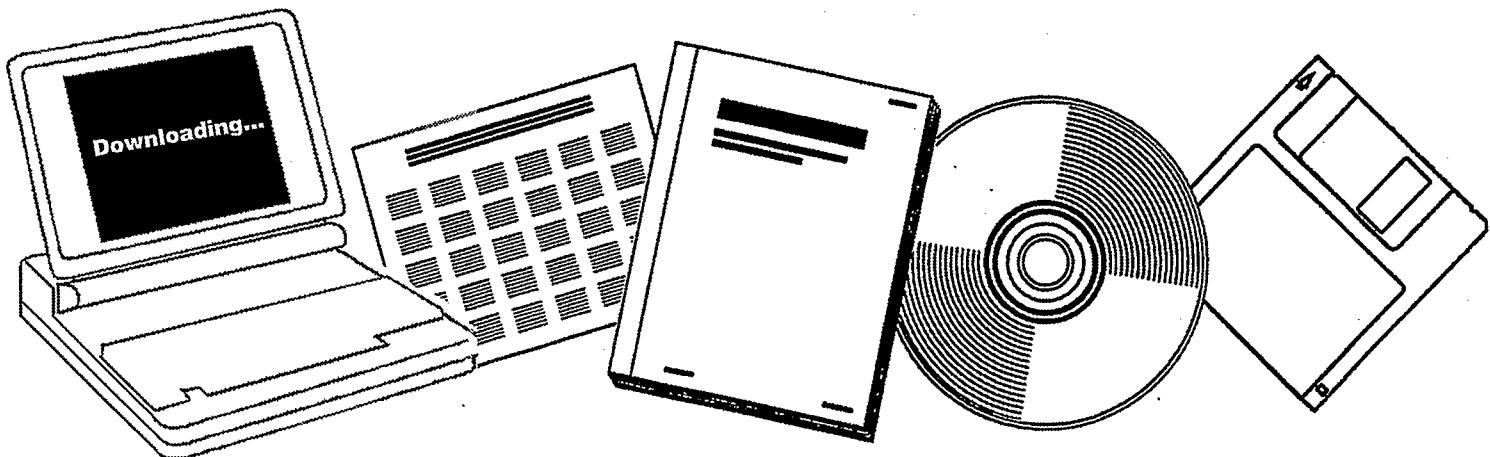
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**TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF
SYNGAS TO ALCOHOLS: TENTH QUARTERLY REPORT
FOR PERIOD DECEMBER 1, 1986 TO FEBRUARY
28, 1987**

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

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

DOE/PC/70780--T6

DE87 007384

Tenth Quarterly Report for Period
December 1, 1986 to February 28, 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

Changes in adsorption sites on Rh/Al₂O₃ catalysts brought about by addition of sodium or by molybdena, was quantified by adsorption of hydrogen and of carbon monoxide. Fresh and used catalyst were tested. XRD was done to rule out the presence of crystalline compound formation. Infrared measurements showed that C-O bond is strengthened slightly by molybdena addition. Hence the enhanced activity of Rh/Mo/Al₂O₃ is caused neither by a greater number of CO sites nor by weakening of CO bond.

The role of sodium in removing surface -OH groups, which in turn changes the distribution of different carbonyl species on the surface, was tested.

Detailed kinetic data for Rh/Mo/Al₂O₃ having different amounts of molybdena were collected. Analysis of rate of formation for primary products were carried out. Activation energies for various reactions were calculated and its implication on the reaction scheme is discussed. The analysis of secondary reactions is underway.

Task 3: Measurement of Surface Composition and Structure**Task 4: Determination of nature of surface complexes****Hydrogen Chemisorption**

To quantify the number of sites, hydrogen chemisorption is used. Hydrogen chemisorption is done on Micromeritics 2100 surface area analyser. Hydrogen is purified with CuO trap and water is removed with zeolite trap. These experiments were done in a static mode. Since CO can be adsorbed as a variety of carbonyl species, CO chemisorption cannot be used to quantify the number of sites. However CO chemisorption can be coupled in a qualitative way with IR to find approximate number and type of CO- adsorption sites. Hydrogen chemisorption is done on used and fresh catalyst.

The striking difference between them is indicated in the table below. The used catalyst was re-reduced at 500C. The irreversibly adsorbed hydrogen decreases quite a lot when the catalyst is used. It is also seen that the difference between the irreversible and reversible hydrogen chemisorption in the used sodium promoted catalyst and the used non-promoted catalyst is not substantial. The amount of irreversible and reversible hydrogen on 3%Rh 2.8%Mo/Al₂O₃ decreases, however the turnover number based on the total Rh content increases by an order of magnitude. This proves that the enhanced activity of Mo-promoted system is not because of physical reasons such as higher dispersion.

Summary of Hydrogen Chemisorption

catalyst	state	Irreversible Hydrogen μ gmoles/gm	Reversible Hydrogen μ gmoles/gm
3%Rh/Al ₂ O ₃	fresh	93.1	57.5
3%Rh/Al ₂ O ₃	used	26.8	14.5
3%Rh 0.67%Na/Al ₂ O ₃	used	23.6	14.2
3%Rh 2%Na/Al ₂ O ₃	fresh	46.0	44.9
3%Rh 2.8%Mo/Al ₂ O ₃	fresh	39.2	39.4

Note:

In 3%Rh 2%Na/Al₂O₃-fresh catalyst the reversible hydrogen decreases with increase in pressure.

145.9 μ gmoles of H₂ = 1 gm of 3% Rh (100% disp), 1H:1Rh

CO chemisorption

CO chemisorption was done in a flow system with TPD capability (figure 1). The CO chemisorption experiments corroborate the fact that it is not the number of CO adsorption sites which makes the difference between Mo promoted and unpromoted Rh/Al₂O₃. The difference in reactivity and CO and hydrogen chemisorption is shown in figure 2. Future experiments are planned to study the effect of state(fresh,used) of catalyst on the CO adsorption on molybdena promoted Rhodium catalyst.

Summary of Carbonmonoxide chemisorption

catalyst	state	CO chemisorbed μmoles/gm at 25C	dispersion %
3%Rh/Al ₂ O ₃	fresh	112.4	39.2
3%Rh 2.8%Mo/Al ₂ O ₃	fresh	74.0	25.8
3%Rh 15% Mo/ Al ₂ O ₃	fresh	28.1	9.8

Note:

Very little effect of temperature cycles is observed i.e. reduction and then CO chemisorption in cycles

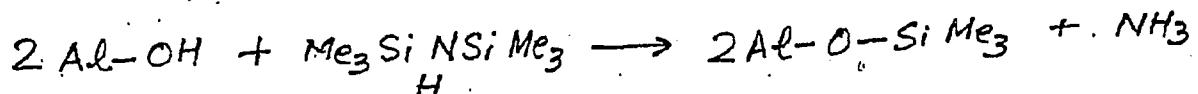
X-Ray Diffraction

X-Ray diffraction was done on used and fresh Molybdena promoted catalyst (3%Rh 2.8% Mo/ Al₂O₃, 3%Rh 7.5%Mo/Al₂O₃ and 3%Rh 15%Mo/Al₂O₃). XRD results show the absence of Rh-crystallite, any Mo-oxide, MoRh₂O₆ Rhodium oxide or Al₂(MoO₄)₃ in the particle size range of 30A to 100A.

Reaction of surface -OH groups with Disilazanes

In the 9th quarterly report, an explanation for the differences in the stabilities of different adsorbed species on the Na-promoted and non-promoted Rh/Al₂O₃ catalyst was put forward. It was proposed that the extent of surface -OH groups play a key role in the interconversion of different carbonyl species on the surface. In the Na-promoted Rh/Al₂O₃, sodium provides a chemical way of blocking or removing -OH groups. This hypothesis was tested by reacting surface -OH groups with disilazanes. Hexamethyldisilazane (HMDS) was selected because of previous work done on Rh/Al₂O₃¹.

The reaction with the surface -OH groups is as follows



HMDS can also bind to the anionic vacancies on Al₂O₃ surface



In the first set of experiments Rh/Al₂O₃ was reduced at 400C under hydrogen and then cooled to 20C. The catalyst is then exposed to vapors of HMDS insitu for 2 hours. It

¹ Zaki M., Gates B.C. and Knozinger H. submitted to J.Phys. Chem

is observed that after the insitu treatment of disilazanes there are no N-H bands. However the two CH_3 bands are clearly seen. It is also observed that the amount of g-dicarbonyl species decrease while the linear species increase. Since CO is adsorbed before exposing the catalyst to HMDS and no N-H bands are seen, we do not expect disilazanes on the metal crystallite. The doublet CH_3 bands are stable upto 300C. Substantial amount of surface -OH groups are present after this treatment. (Figure 3 and 4).

The second set of experiments were done by treating the support with excess HMDS for 24 hours. In this case most of the surface -OH reacts with HMDS as seen by the absence of the surface -OH bands.

Interpretation of Infrared shifts for CO chemisorbed on Mo-promoted Rh/ Al_2O_3

The shifts in CO-adsorbed on Molybdena promoted Rh/ Al_2O_3 were reported in the ninth quarterly report. These shifts can be explained using F and G² matrix theory of vibrational spectroscopy. The vibrational spectra of a g-dicarbonyl specie has two relevant stretching force constants (neglecting the coupling between the metal vibrations and the adsorbate stretches and also the coupling between the stretching and bending force fields). $k(\text{CO})$ is the vibrational force constant for each CO bond and $k(\text{CO},\text{CO}')$ is the force field parameter for coupling between the stretches of the adjacent CO ligands on the g-dicarbonyl specie.

The results of the calculations are summarised below

catalyst	Experimental data antisymmetric stretch cm^{-1}	symmetric stretch cm^{-1}	Calculations $k(\text{CO})$ Nm^{-1}	$k(\text{CO},\text{CO}')$ Nm^{-1}
3%Rh/ Al_2O_3 fresh	2012	2084	1694.3	59.6
3%Rh 7.5%Mo/ Al_2O_3 fresh	2027	2093	1714.1	54.9

The C-O bond is strengthened on Molybdena promotion. Hence the enhanced activity is caused neither by greater number of CO sites nor by weakening of the CO bond.

Task 5: Reaction mechanism by isotopic tracers and kinetics.

Kinetic analysis of promoted Rh/ Al_2O_3

The kinetic analysis of Molybdena promoted Rh/ Al_2O_3 is done to investigate the effect of process parameters on the activity and selectivity of the catalyst. The catalyst are remarkably stable after an initial transient of about 8 hours. The kinetic analysis is done in 4 stages.

Stage I:

Identification of primary and secondary products and analysis of overall kinetics.

Stage II:

Kinetic analysis of primary products.

² Braterman P. S., " Metal Carbonyl Spectra", Academic Press, 1975.

Stage III:

Kinetic analysis of secondary products and analysis of complete reaction network.

Stage IV:

Estimation of Activation Energies and effect of temperature on the reaction network.

Stage I:

Table 2,3 and 4 show data for 3%Rh15%Mo/Al₂O₃ at three different temperatures. The increase in the amount of hydrocarbons is evident when the temperature is high. The x and y values for the rate expression for conversion of CO to all products

$$R_{CO} = k * (pH_2)^x * (pCO)^y$$

for 3%Rh15%Mo/Al₂O₃ are x ≈ 0.8, y ≈ 0.0 compared to x ≈ 0.6 and y ≈ -0.3 for non promoted systems. However it should be noted that this x and y values are at different temperatures to get the same conversion range. The shift in the values of x and y reflect the shift in the product distribution. Higher amounts of oxygenates are formed at lower temperature

The %Carbon selectivity to C₂₊ oxygenates decreased slightly with increase in temperature. This result is surprising because CH_x species are needed to form C₂₊ oxygenates and the amount of CH_x species should increase with temperature. This result indicates that CO insertion step is the rate controlling step in formation of C₂₊ oxygenates.

Another set of kinetic data is reported in table 2 . This data is made up of two set of runs. The effect of pressure was investigated at same mass flow rate and at same actual contact time. There was very little effect on of pressure on the formation of hydrocarbons. The fraction of oxygenates and CO₂ increased while the secondary products decreased.

Effect of CO/H₂ ratio and space time on the activity and product distribution characteristics of the catalyst

This set of experiments were done for 3%Rh7.5%Mo/Al₂O₃. The catalyst was reduced at 500C for 1 hr under 50scc/min of flowing hydrogen. The product distribution and activity of the catalyst was measured at fixed temperature and pressure and at a range of GHSV and CO/H₂ ratio. It was surprising to see that the overall conversion follows pseudo first order kinetics(see figure)

The table below shows the pseudo first order rate constants

3%Rh 7.5%Mo/ Al₂O₃ , 200C, 450 psi

CO/H ₂	k(sec ⁻¹)
2	0.00832 ± 0.00032
1	0.02248 ± 0.00013
1/2	0.04480 ± .0015
1/3	0.0623 ± 0.0028
1/5	0.1101 ± 0.0033

The data collected for 3%Rh 7.5% Mo/Al₂O₃ was plotted to see the effect on CO/H₂ on the nature of the product and the ratio of the pseudo first order rate constants. This methodology of analysing data was discussed in 8th quarterly report. The following conclusions were reached.

CH_4 is a primary product for $\text{CO}/\text{H}_2 \leq 2$. This implies the formation of CH_4 at high CO/H_2 ratio has two slow steps compared to one at low CO/H_2 ratio

The intercepts for the plot of (mole fraction of specie)/conv of CO against conversion of CO are listed on the next page. The intercepts are the ratio of the pseudo first order rate constant for the slow step in the formation of the specie to the sum of pseudo first order rate constant for the consumption of the parent specie.

3%Rh 7.5%Mo / Al_2O_3 , 200C

CO/H_2	pCO psi	pH ₂ psi	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

* - inverse S-shaped curve

Stage II:

The rate of formation of primary product is found experimentally at two different GHSV. The rate of primary product should be independant of GHSV. Hence the consistency of rate of the specie is taken as a test of the experimental method and the analysis of Stage I. The rate is found at 18 different combinations of pCO and pH₂. The above experiment is repeated at three different temperatures. A sample table is given below for 3%Rh 15% Mo / Al_2O_3 at 210C.

$$\text{Rate}_{\text{specie}} = k * (\text{pCO})^y * (\text{pH}_2)^x$$

Specie	ln(k)	y	x
MeOH	-16.895 ± 0.162	-0.005 ± 0.113	1.527 ± 0.096
CO	-10.301 ± 0.091	-0.030 ± 0.064	0.724 ± 0.054
CO ₂	-10.712 ± 0.091	-0.040 ± 0.064	0.377 ± 0.054
CH ₄	-7.676 ± 0.126	-0.323 ± 0.088	1.021 ± 0.075

Table 4 shows comparison of x and y with different systems reported in literature for methane and methanol. Table 2,3 and 4 show preliminary kinetic data for 3%Rh 7.5%Mo / Al_2O_3 and 3%Rh 15%Mo Al_2O_3 .

Stage III:

The first approach is to use H-J-B method with models which are linear in parameter space. This method has the advantage of not needing any initial guess. Here the rate expression for primary products from Stage II are used. The second approach is to use Spline approximation combined with non-linear regression routines³. The advantage of this method are (i) Jacobians needed for the next guess can be found very easily by using the properties of spline and (ii) it has a variable smoothing parameter. A couple of networks have been tried using the first approach and the second approach is in the stage of writing programs.

Stage IV

An estimate of activation energy is made for different products and overall reaction. This estimate is based on the assumption that for small conversion the amount of CO converted is approximately proportional to the rate constant at a given contact time and that the selectivity is quite independent of the contact time. The temperature dependence of the actual rate constant is not very different from the temperature dependence of the pseudo first order rate constant. Figure 5 shows a semi-log plot of % C in a specie against $1/T$ for 3%Rh 7.5% Mo /Al₂O₃ at 450 psi.

The table below lists the activation energies from figure 5.

specie	Approximate activation energies	
	ln(A*b)	E _{act} Kcal/gmol
CO	24.998 ± 0.067	21.62 ± 0.92
CO ₂	23.897 ± 0.084	21.94 ± 0.66
CH ₄	33.848 ± 0.196	32.39 ± 2.6
Cloxyg	19.707 ± 0.482	17.23 ± 0.66
C ₂ oxyg	25.562 ± 0.178	24.28 ± 2.41
totoxyg	21.346 ± 0.062	18.58 ± 0.85

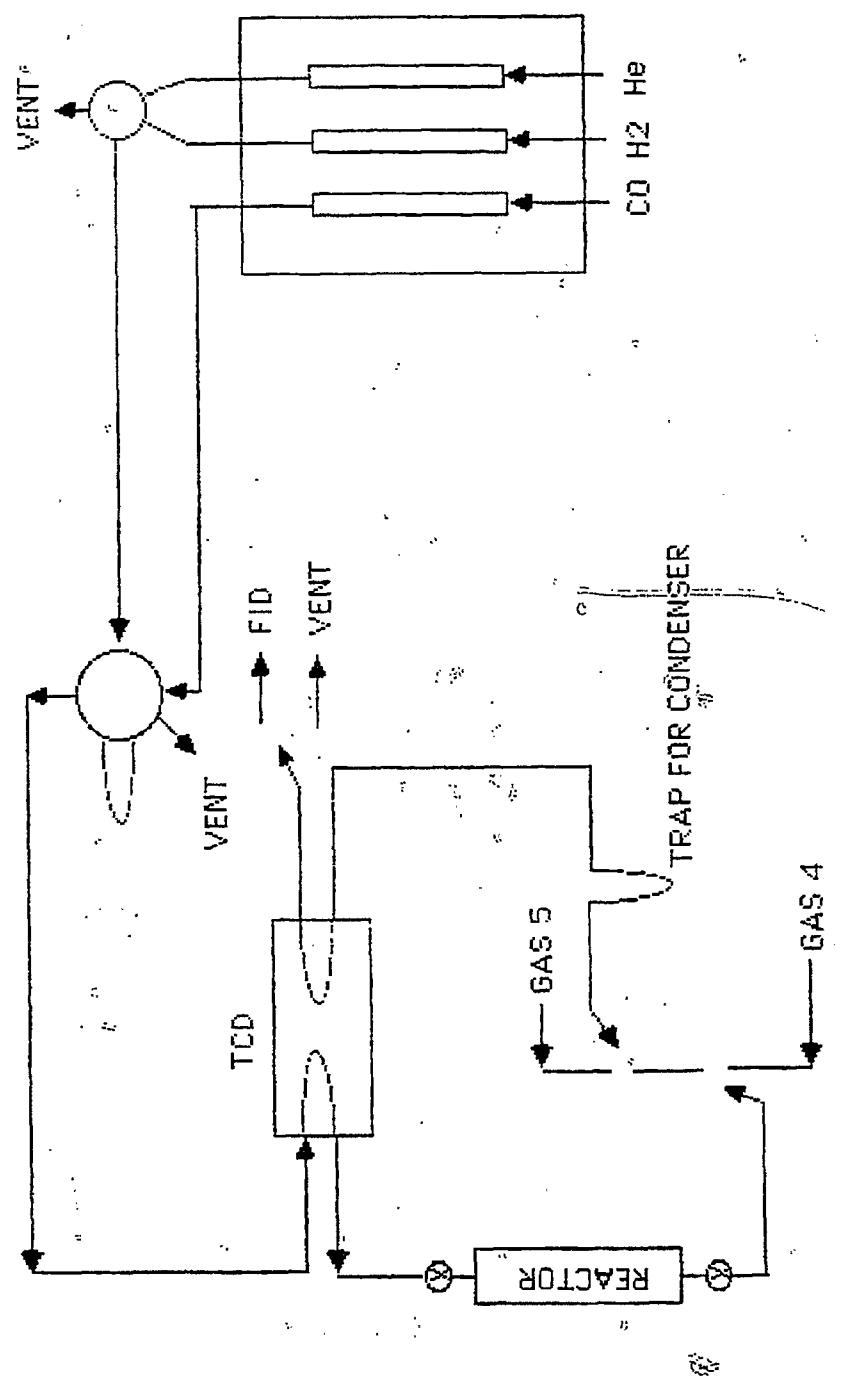
b- arbitrary constant

The higher E_{act} for methane compared to oxygenates is consistent with relatively increased methane formation at higher temperatures and, conversely higher relative oxygenates formation at lower temperature (Figure 6).

³ Yermakova A., Vajda S. and Valko P., Applied Catalysis, 2(1982)139.

TPD/CHROMATOGRAPHIC APPARATUS FLOW DIAGRAM

Figure 1:



Comparison of CO chem and turnover

3%Rh x%Mo /Al₂O₃

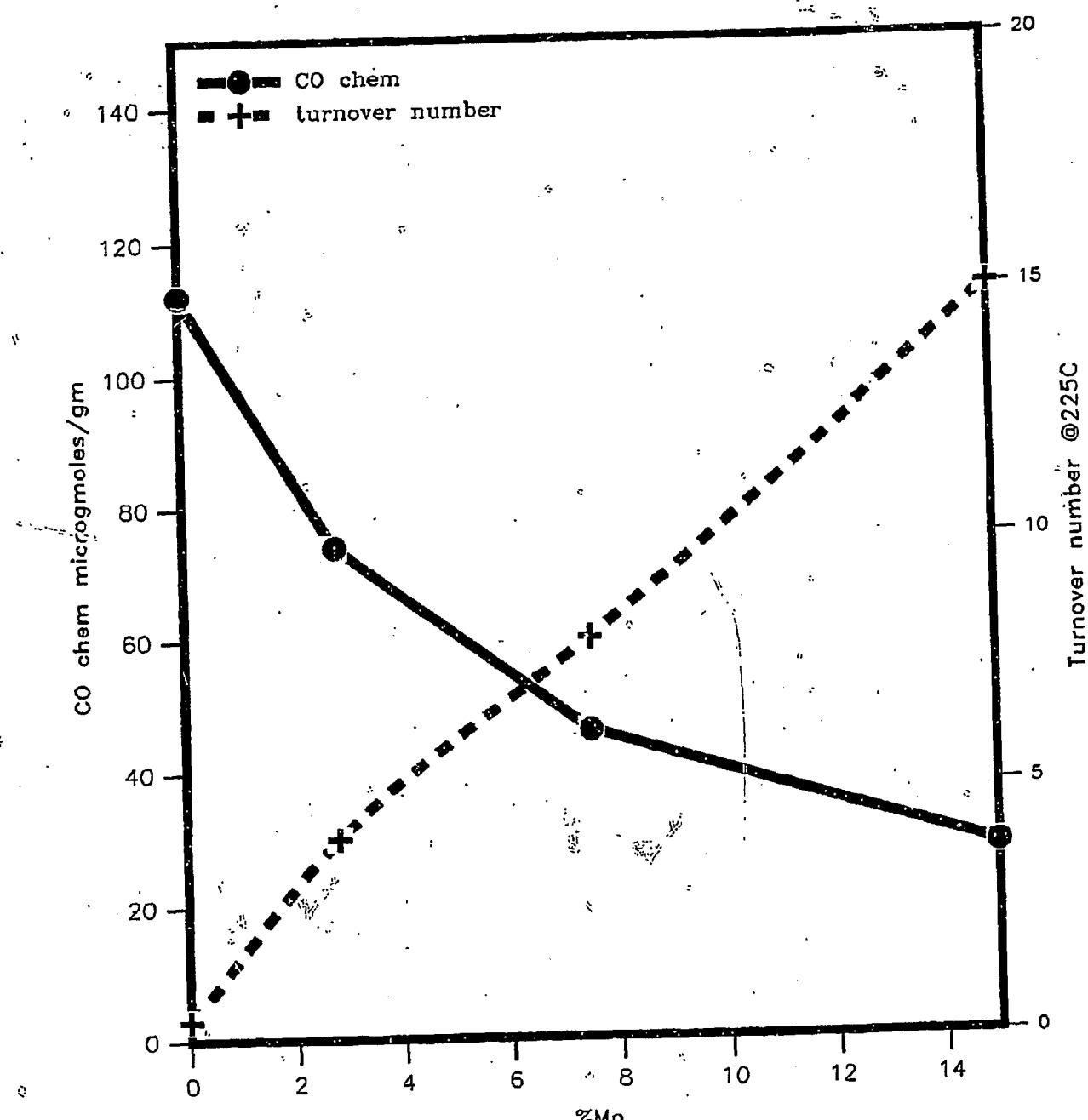


Figure 2

Normalised to total Rh.

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(Fig 3)

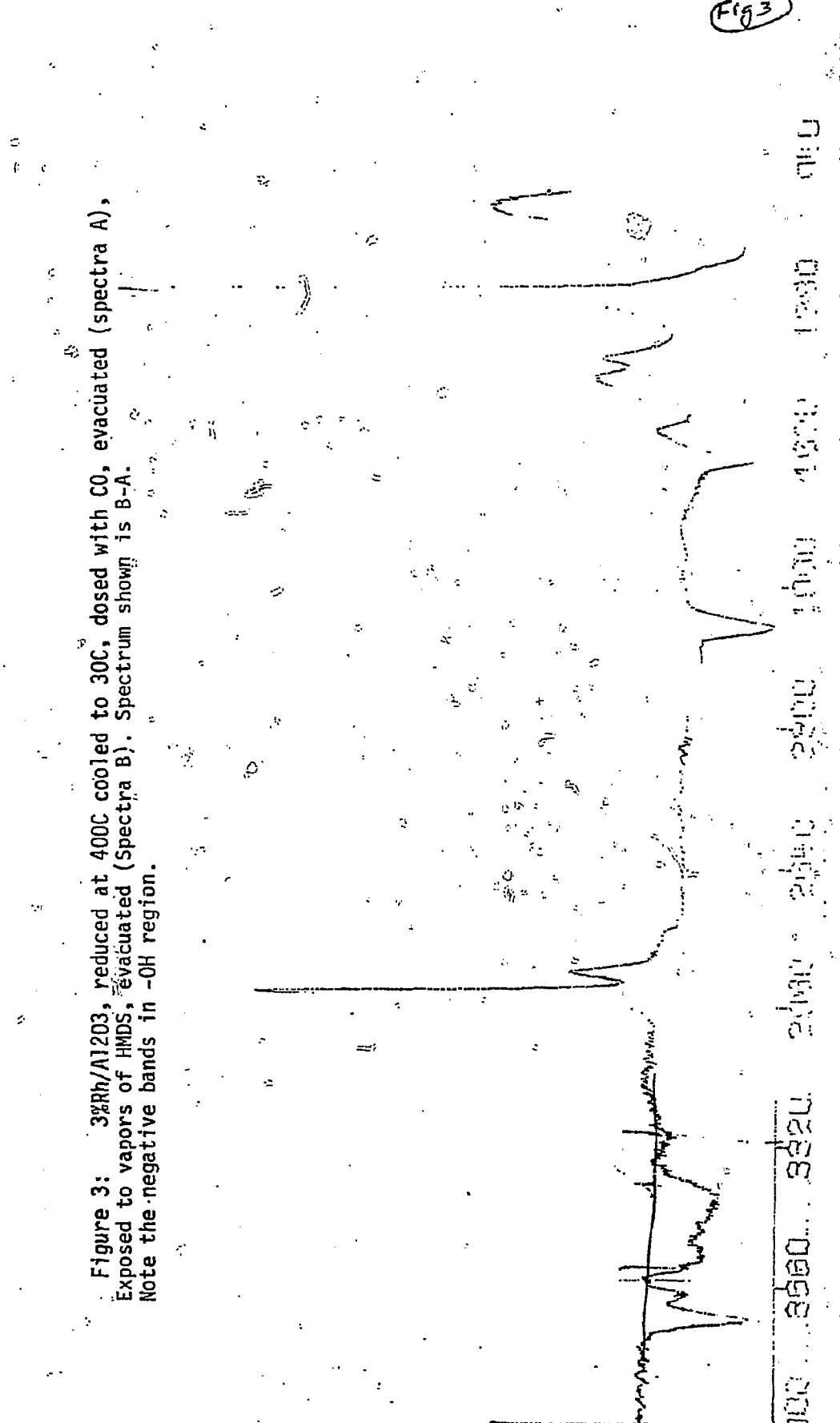


Figure 3: 3%Rh/A1203, reduced at 400°C cooled to 300°C, dosed with CO, evacuated (spectra A), Exposed to vapors of HMDS, evacuated (Spectra B). Spectrum shown is B-A.
Note the negative bands in -OH region.

Figure 4: Reaction of Rh/Al2O3 with HMDS
Note the absence of N-H bands.

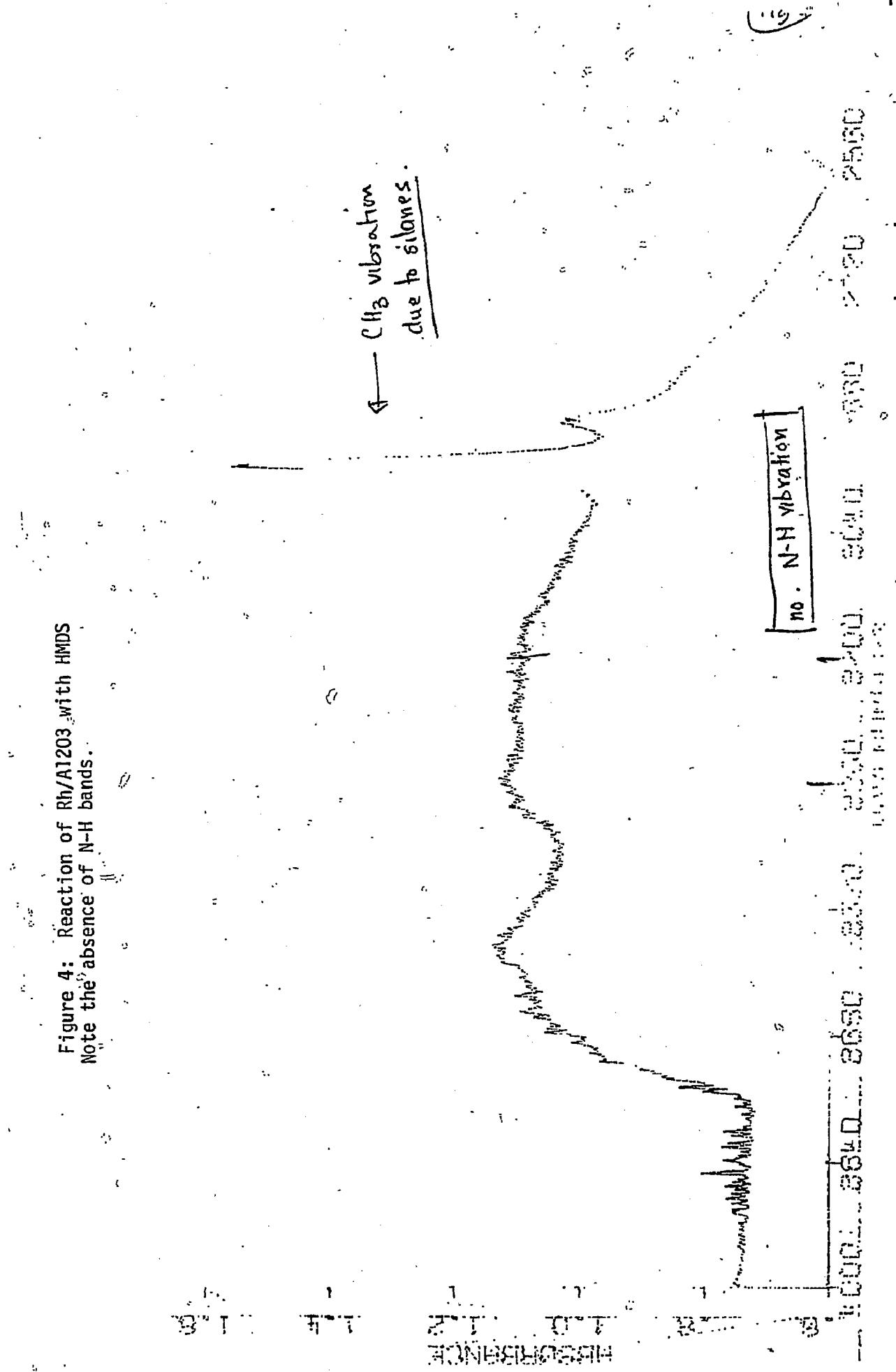
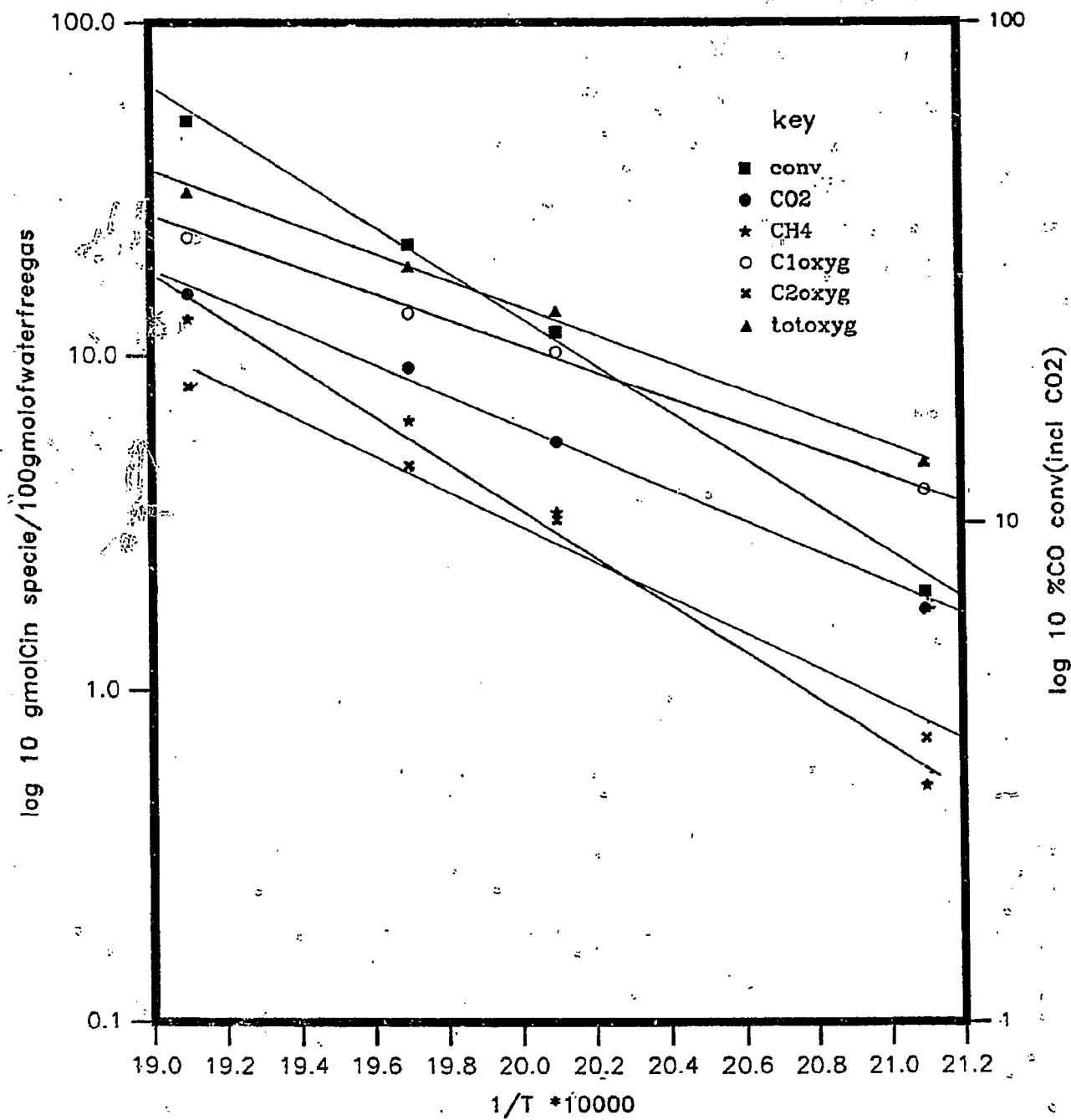


Figure 5:

Approximate activation energies

3%Rh7.5%Mo Al2O₃ 450 psi CO/H₂=1:2

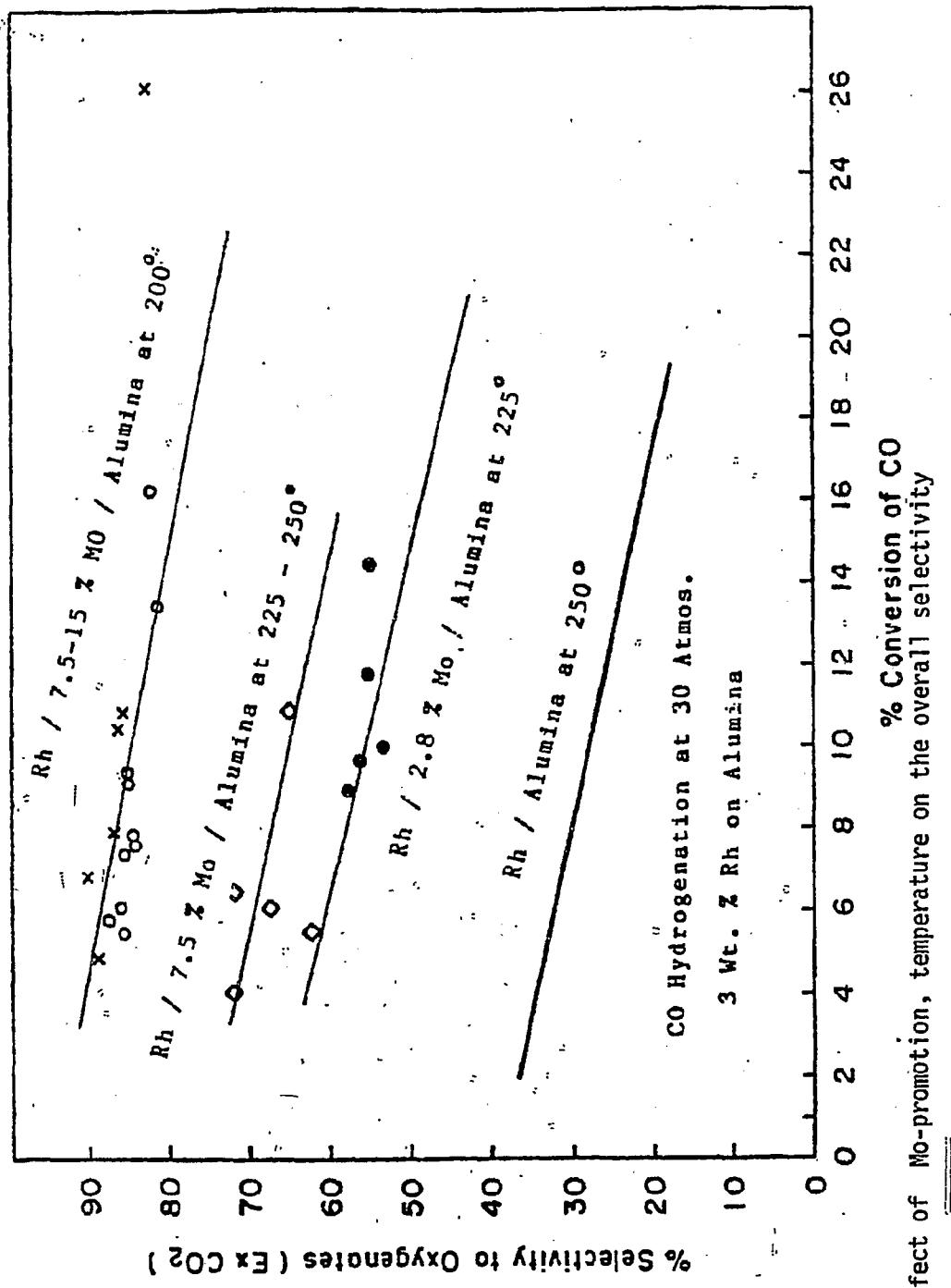


data wrt 3000GHSV

March 19,1987.

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Figure 6:



Effect of Mo-promotion, temperature on the overall selectivity

Table 1 Page 1

Table 1 Page 2

Table 1 Page 3

Hydro_CX		oxyg_CX		turnover_Inrate		In(ppm)		ln(ppm)		Constant		Regression Output:	
C1	C2	C1	C2	no.	sec-1	no.	sec-1	no.	sec-1	no.	sec-1	no.	sec-1
9.2	3.5	77.0	10.2	2.04E-03	-7.00E-02	5.010635	5.703782	Std Err of Y Est		0.055443		0.055443	
9.0	3.6	77.1	10.2	2.05E-03	-7.00E-02	5.010635	5.703782	R-Squared		0.96776		0.96776	
9.2	3.4	76.8	10.7	2.10E-03	-6.98E-02	5.010533	5.703782	No. of Observations		20		20	
9.0	3.3	77.9	10.3	2.08E-03	-6.98E-02	5.010635	5.703782	Degrees of Freedom		17		17	
0.7	3.1	76.9	10.8	2.02E-03	-6.98E-02	5.010635	5.703782						
9.2	3.2	78.3	10.2	2.04E-03	-7.00E-02	5.010635	5.703782	X Coefficient(s)		-2.344431		-1.87058	
9.2	3.1	78.0	9.9	2.00E-03	-7.02E-02	5.010535	5.703782	Std Err of Coef		0.181915		0.208945	
9.5	3.1	78.6	9.6	1.96E-03	-7.02E-02	5.010535	5.703782	Degrees of Freedom		3.004195		3.004195	
8.0	2.9	79.5	10.4	2.05E-03	-7.00E-02	5.010635	5.703782	Constant		0.104399		0.104399	
7.9	3.0	79.5	10.4	2.05E-03	-7.00E-02	5.010635	5.703782	Std Err of Y Est		0.104399		0.104399	
0.3	3.0	79.7	6.3	3.30E-03	-6.49E-02	5.722953	5.821565	R-Squared		0.833641		0.833641	
3.0	3.0	79.2	8.7	3.09E-03	-6.52E-02	5.722953	5.821565	No. of Observations		13		13	
3.4	3.3	80.0	7.2	3.69E-03	-6.15E-02	5.722953	5.821565	Degrees of Freedom		10		10	
9.0	3.0	79.0	8.2	3.12E-03	-6.58E-02	5.722953	5.821565						
9.3	8.8	79.9	9.2	3.09E-03	-6.60E-02	5.722953	5.821565	X Coefficient(s)		-1.117479		-0.92029	
9.8	2.9	80.6	2.6	2.97E-03	-6.60J36	5.722953	5.821565	Std Err of Coef		0.478833		0.547571	
6.9	3.7	76.7	12.6	1.51E-03	-7.31E-02	5.703782	5.010635	Constant		-6.105614		0.054136	
5.9	3.4	79.3	11.3	1.55E-03	-7.28E-02	5.703782	5.010635	Std Err of Y Est		0.307153		0.521839	
5.3	3.3	79.3	11.6	1.92E-03	-7.44E-02	5.703782	5.010635	R-Squared		0.818330		0.818330	
3.8	2.6	81.2	12.3	1.52E-03	-7.29E-02	5.703782	5.010635	No. of Observations		17		17	
6.6	2.8	81.5	9.0	5.23E-04	-6.38E-02	5.010635	5.703782	Degrees of Freedom		14		14	
6.2	2.6	82.5	8.6	1.05E-04	-6.23E-02	5.010635	5.703782						
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	X Coefficients		-0.316911		0.317625	
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	Std Err of Coef.		0.307153		0.521839	
0.2	0.0	82.1	0.1	8.31E-04	-5.63E-02	5.722953	5.821565	Constant		-6.105614		0.054136	
7.3	0.3	82.1	7.5	7.92E-04	-5.63E-02	5.722953	5.821565	Std Err of Y Est		0.307153		0.521839	
6.2	2.1	84.1	7.5	7.92E-04	-5.63E-02	5.722953	5.821565	R-Squared		0.818330		0.818330	
6.2	2.1	84.1	7.4	7.92E-04	-5.63E-02	5.722953	5.821565	No. of Observations		17		17	
3.5	1.6	85.0	6.0	6.26E-04	-6.18E-02	5.703782	5.010635	Degrees of Freedom		14		14	
1.1	1.4	84.5	10.1	5.37E-04	-6.24E-02	5.010635	5.703782						
2.0	1.1	85.0	11.1	5.74E-04	-6.24E-02	5.010635	5.703782	X Coefficients		-0.316911		0.317625	
3.6	1.4	82.9	11.6	4.77E-04	-6.30E-02	5.010635	5.703782	Std Err of Coef.		0.307153		0.521839	
9.5	1.1	82.9	12.1	4.71E-04	-6.30E-02	5.010635	5.703782						
11.2	3.5	75.7	10.9	9.8E-05	-5.93E-02	5.010635	5.703782	Constant		-0.316911		0.317625	
11.0	3.5	75.8	9.3	6.02E-05	-5.94E-02	5.010635	5.703782	Std Err of Y Est		0.307153		0.521839	
11.2	3.6	75.8	9.3	6.02E-05	-5.94E-02	5.010635	5.703782	R-Squared		0.818330		0.818330	
11.3	3.4	76.1	8.8	6.02E-05	-5.94E-02	5.010635	5.703782	No. of Observations		17		17	
10.4	3.9	77.2	9.0	6.25E-05	-5.88E-02	5.010635	5.703782	Degrees of Freedom		16		16	
10.1	3.7	77.0	9.0	6.14E-05	-5.80E-02	5.010635	5.703782						
10.0	3.5	77.1	9.2	6.07E-05	-5.81E-02	5.010635	5.703782	X Coefficients		-0.316911		0.317625	
9.4	3.2	78.2	9.0	6.35E-05	-5.81E-02	5.010635	5.703782	Std Err of Coef.		0.307153		0.521839	
7.6	2.9	80.9	8.6	7.20E-05	-5.74E-02	5.010635	5.703782						
10.3	3.1	78.5	8.4	7.39E-05	-5.74E-02	5.010635	5.703782	Constant		-0.316911		0.317625	
9.2	3.4	78.5	8.6	7.41E-05	-5.74E-02	5.010635	5.703782	Std Err of Y Est		0.307153		0.521839	
9.5	4.2	78.4	10.3	4.67E-05	-5.13E-02	5.010635	5.703782	R-Squared		0.818330		0.818330	
9.6	3.9	78.4	11.0	4.73E-05	-5.13E-02	5.010635	5.703782	No. of Observations		17		17	

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C1		C2		C3		C4		C5		C6		C7		C8		C9		C10		C11		C12		C13		C14		C15		C16		C17		C18		C19		C20		C21		C22		C23		C24	
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Table 2 Page 6

Regression Output:		Date	CO ₂ -Incrate	EMEDEH	DEMEDEH												
		10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14	10-22-14				
df	17	Est.	0.0435110	0.92E-04	-0.123	0.900	2.360	0.069	3.751	0.232	207.857	1.43.662	33.522	7.06E-08			
d	16	Residuals	0.96735	2.09E-04	-0.470	1.046	1.399	0.059	1.259	0.097	297.735	5.140	8.04E-08	0.086			
of Freedom	17	Residuals	20	2.09E-04	-0.472	0.951	1.286	0.065	1.305	0.747	297.503	1.47.166	3.537	7.38E-08	0.080		
df	17	Residuals	20	2.09E-04	-0.679	0.294	0.956	0.049	1.054	0.451	1.46.312	71.980	4.767	1.89E-07	0.094		
df	17	Residuals	20	2.09E-04	-0.657	0.203	0.943	0.049	1.077	0.430	1.46.951	71.971	5.145	1.85E-07	0.097		
df	17	Residuals	20	2.09E-04	-0.647	0.164	0.945	0.045	1.180	0.461	1.22.173	109.454	4.269	1.20E-07	0.062		
df	17	Residuals	20	2.09E-04	-0.639	0.159	0.943	0.043	1.177	0.452	222.252	109.486	4.326	1.10E-07	0.060		
df	17	Residuals	20	2.09E-04	-0.621	0.595	1.159	0.043	1.177	0.452	222.252	109.486	4.326	1.10E-07	0.060		
df	17	Residuals	20	2.09E-04	-0.603	0.729	1.145	0.049	1.056	0.495	221.509	71.365	5.204	2.07E-07	0.079		
df	17	Residuals	20	2.09E-04	-0.585	0.648	1.204	0.041	1.144	0.685	222.003	71.256	5.395	1.85E-07	0.077		
df	17	Residuals	20	2.09E-04	-0.444	1.226	1.497	0.077	1.347	0.351	335.767	100.500	4.383	1.01E-07	0.179		
df	17	Residuals	20	2.09E-04	-0.435	1.101	1.464	0.077	1.279	0.920	335.791	108.649	4.042	9.64E-08	0.078		
df	17	Residuals	20	2.09E-04	-0.435	1.169	1.464	0.079	1.273	0.951	335.017	108.660	4.109	9.53E-08	0.076		
df	17	Residuals	20	2.09E-04	-0.437	2.04E-04	0.495	0.051	1.115	0.310	147.292	147.952	3.576	7.725E-03	0.094		
df	17	Residuals	20	2.09E-04	-0.437	1.80E-04	0.249	0.924	0.051	1.094	0.370	147.101	147.944	2.540	6.03E-03	0.092	
df	17	Residuals	20	2.09E-04	-0.437	1.79E-04	0.257	0.954	0.052	1.021	1.112	-0.119	110.405	223.001	-4.604	6.14E-03	0.080
df	17	Residuals	20	2.09E-04	-0.437	1.90E-04	0.621	0.163	0.021	0.967	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160	0.627	0.023	0.967	-0.116	110.624	224.026	-4.103	5.80E-03	0.065	
df	17	Residuals	20	2.09E-04	-0.437	1.759	0.160</										

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Model	Mech.	ELOI	Scallop	Height	Depth	ECHO	CSDM	Model	Lime	p-BuOH	I-BuOH	TOTALOX YZC2+OxH		XHIE E	
												CZ-CO2Proof	Total	Small Cr.	
61.3	0.0	2.4	0.0	2.4	0.0	0.0	0.0	61.3	0.0	0.0	0.0	87.3	11.8	9.1E-	
61.4	0.0	2.4	0.0	2.4	0.0	0.0	0.0	61.4	0.0	0.0	0.0	91.0	7.6	9.4E-	
63.4	0.0	2.4	0.0	2.4	0.0	0.0	0.0	63.4	0.0	0.0	0.0	91.0	8.2	9.4E-	
65.2	0.0	1.9	0.0	1.9	0.0	0.0	0.0	65.2	0.0	0.0	0.0	92.1	6.6	7.0E-	
65.4	0.0	1.9	0.0	1.9	0.0	0.0	0.0	65.4	0.0	0.0	0.0	91.3	8.7	7.7E-	
68.3	0.0	1.3	0.0	1.3	0.0	0.0	0.0	68.3	0.0	0.0	0.0	90.3	8.2	1.0E-	
68.5	0.0	1.3	0.0	1.3	0.0	0.0	0.0	68.5	0.0	0.0	0.0	89.6	8.5	1.1E-	
69.1	0.0	1.3	0.0	1.3	0.0	0.0	0.0	69.1	0.0	0.0	0.0	89.7	8.4	1.2E-	
70.1	0.0	1.3	0.0	1.3	0.0	0.0	0.0	70.1	0.0	0.0	0.0	85.7	9.4	1.2E-	
70.5	0.0	1.3	0.0	1.3	0.0	0.0	0.0	70.5	0.0	0.0	0.0	85.7	7.9	1.2E-	
70.6	0.0	1.3	0.0	1.3	0.0	0.0	0.0	70.6	0.0	0.0	0.0	89.4	10.5	1.2E-	
70.7	0.0	1.3	0.0	1.3	0.0	0.0	0.0	70.7	0.0	0.0	0.0	89.3	10.5	6.1E-	
70.8	0.0	1.3	0.0	1.3	0.0	0.0	0.0	70.8	0.0	0.0	0.0	89.3	10.5	6.1E-	
75.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	75.3	0.0	0.0	0.0	90.5	7.8	2.3E-	
75.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	75.7	0.0	0.0	0.0	94.4	2.4	2.4E-	
76.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	76.1	0.0	0.0	0.0	90.0	9.0	9.0E-	
76.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	76.5	0.0	0.0	0.0	89.2	9.2	9.2E-	
76.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	76.7	0.0	0.0	0.0	89.2	9.2	9.2E-	
77.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77.1	0.0	0.0	0.0	84.3	8.7	1.3E-	
77.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77.4	0.0	0.0	0.0	80.8	9.0	1.3E-	
77.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77.7	0.0	0.0	0.0	80.4	9.1	1.3E-	
78.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	78.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
78.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	78.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
79.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	79.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
79.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	79.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
80.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	80.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
80.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	80.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
80.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	80.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
81.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	81.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
81.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	81.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
81.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	81.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
82.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
82.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
82.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
83.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	83.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
83.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	83.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
84.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	84.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
84.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	84.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
84.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	84.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
85.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	85.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
85.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	85.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
86.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	86.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
86.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	86.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
86.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	86.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
87.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	87.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
87.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	87.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
88.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	88.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
88.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	88.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
88.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	88.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
89.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	89.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
89.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	89.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
90.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
90.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
90.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
91.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	91.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
91.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	91.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
92.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	92.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
92.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	92.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
92.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	92.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
93.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	93.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
93.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	93.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
94.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
94.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
94.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
95.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	95.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
95.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	95.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
96.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	96.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
96.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	96.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
96.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	96.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
97.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
97.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
98.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
98.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
98.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
99.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	99.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
99.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	99.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
100.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.1	0.0	0.0	0.0	89.4	7.7	1.4E-	
100.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.5	0.0	0.0	0.0	89.4	7.7	1.4E-	
100.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.9	0.0	0.0	0.0	89.4	7.7	1.4E-	
101.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	101.3	0.0	0.0	0.0	89.4	7.7	1.4E-	
101.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	101.7	0.0	0.0	0.0	89.4	7.7	1.4E-	
102.1	0.0	0.0	0.0	0.0	0.0										

Table 3 Page 4

S/N	NAME CO CODE Line1	NAME CO CODE Line2	CODE LINE		CODE LINE		CODE LINE		CODE LINE		CODE LINE	
			1	2	3	4	5	6	7	8	9	10
11.0	9.1E-04	32.0 Mettice sprayer			9.2	3.5			0.0	0.0	77.0	
7.6	9.3E-04	24.5			7.5	1.9	0.0	0.0	64.9	0.0	64.9	
6.1	9.4E-04	24.1			7.6	1.3	0.0	0.0	63.6	0.0	63.6	
3.5	7.0E-04	25.1			6.3	1.6	0.0	0.0	64.2	0.0	64.2	
3.7	7.7E-04	22.9			7.1	1.6	0.0	0.0	63.5	0.0	63.5	
3.1	1.0E-03	25.0				0.5	1.2	0.0	0.0	0.0	0.0	0.0
3.3	1.1E-03	23.9				7.7	2.5	0.0	0.0	0.0	0.0	0.0
3.4	1.2E-03	29.3				8.1	2.1	0.0	0.0	0.0	0.0	0.0
3.4	1.2E-03	24.6				8.0	2.2	0.0	0.0	0.0	0.0	0.0
7.8	1.3E-03	24.6				8.4	2.3	0.0	0.0	0.0	0.0	0.0
10.9	6.1E-04	22.7 Mettice and Mettice pearls fused, Mettice shoulder sprayer w/ 1523, Ethyl heat: S				6.4	4.5	0.0	0.0	0.0	0.0	0.0
7.0	2.3E-04	49.1 Hisoni, ELCN and Hisoni not seen, very transparent				5.1	4.4	0.0	0.0	0.0	0.0	0.0
5.1	2.4E-04	22.7				2.0	3.1	0.0	0.0	0.0	0.0	0.0
9.0	9.7E-04	22.6				7.6	1.5	0.0	0.0	0.0	0.0	0.0
9.1	9.4E-04	22.6				0.1	2.7	0.0	0.0	0.0	0.0	0.0
9.7	1.3E-03	16.9				6.8	8.9	0.0	0.0	0.0	0.0	0.0
9.0	1.3E-03	20.1				7.0	2.9	0.0	0.0	0.0	0.0	0.0
9.1	1.5E-03	18.7				7.1	2.5	0.0	0.0	0.0	0.0	0.0
7.7	1.4E-03	19.8				7.7	2.7	0.0	0.0	0.0	0.0	0.0
9.1	7.1F-04	25.1					7.6	2.1	0.0	0.0	0.0	0.0
9.3	7.1H-04	24.9					7.1	3.1	0.0	0.0	0.0	0.0
10.3	4.9E-04	30.0 Mettice sprayer					9.1	2.6	0.0	0.0	0.0	0.0
6.9	1.5E-04	100.0 Mettice sprayer					EPR	EPR	EPR	EPR	EPR	EPR

Table 3 Page 5

Table 3 Page 6

Element	Element	Element	Element						
Det	Det	Det	Det						
0.900	2.360	0.083	3.251	0.392	292.657	143.652	38.522	7.05E-09	0.250
1.413	0.446	1.425	0.604	298.175	147.102	4.781	5.89E-08	0.076	
1.400	0.048	1.438	0.616	298.154	147.091	4.731	5.96E-08	0.094	
0.773	0.824	0.123	150.546	98.414	3.603	9.52E-09	0.050		
0.373	0.002	0.127	0.734	0.417	98.450	3.394	3.86E-08	0.056	
0.384									
1.420	1.957	0.081	2.135	0.704	392.344	195.715	6.150	4.60E-08	0.119
1.571	1.903	0.094	2.051	0.713	392.014	195.687	4.556	5.05E-08	0.121
2.114	0.170	3.103	1.111	495.584	243.590	5.20	4.74E-08	0.121	
2.210	2.599	0.137	2.971	0.979	195.159	203.021	6.169	3.60E-08	0.130
2.214	2.569	0.142	2.980	0.945	195.099	243.341	6.101	3.63E-08	0.116
0.117	0.307	0.009	0.264	0.203	98.568	49.590	2.918	2.40E-07	0.130
0.001	0.010	0.000	0.120	-0.006	10.000	4.021	-7.153	2.23E-06	0.001
0.004	0.014	0.000	0.011	0.000	9.194	4.176	2.041	7.63E-05	0.002
1.383	1.357	0.024	1.363	0.195	292.659	142.170	3.975	7.95E-08	0.057
0.890	1.342	0.055	1.359	0.749	292.529	147.152	3.072	6.35E-08	0.136
1.765	1.697	0.114	1.519	244.736	192.061	1.303	1.49E-07	0.093	
1.559	1.676	0.105	1.547	1.059	245.645	197.762	1.825	1.31E-07	0.063
4.325	1.059	0.152	1.452	1.261	496.191	245.683	2.725	3.84E-08	0.031
1.950	1.029	0.112	1.210	1.157	495.575	245.514	2.965	3.22E-08	0.130
0.529	1.049	0.089	1.112	0.470	198.054	97.223	4.006	1.37E-07	0.174
0.494	1.065	0.095	1.096	0.490	193.211	97.215	4.552	1.25E-07	0.177
0.156	0.216	0.012	0.524	0.187	99.347	40.373	10.159	3.28E-07	0.168
0.127	0.589	0.012	0.642	0.108	91.457	44.564	0.283	3.40E-07	0.142

Table 4:

COMPARISON OF POWER LAW RATE PARAMETERS

$$\text{RATE} = A \cdot e^{-E/RT} \cdot P_{H_2}^x \cdot P_{CO}^y$$

CATALYST	CH4		MeOH		REFERENCE
	x	y	x	y	
Rh / SiO ₂	0.57	-0.2			a
Rh / SiO ₂	0.7	-0.2	1.3	-0.1	b
Rh / La ₂ O ₃	0.8	-0.6	1.1	0.1	c
Rh / La ₂ O ₃	0.9	-0.5	1.5	-0.1	b
Rh/Mo/Al ₂ O ₃	1.0	-0.3	2.0	0	U. Del.
a F. Solymosi, I. Tombacz, M. Kocis. J.Catal., 75 (1982) 78					
b R.P. Underwood, A.T. Bell. Applied Catal., 21 (1986) 157					
c M. Ichikawa, K. Shikakura. Proc. 7th Int. Congr. Catal. Tokyo (1980)					
U. Del. C. Sudakar, N. Bhore, K. Bischoff, W. Manogue, A. Mills					

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