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TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS. EIGHTH QUARTERLY REPORT, JUNE 1, 1986-AUGUST 31, 1986

DELAWARE UNIV., NEWARK. CENTER FOR
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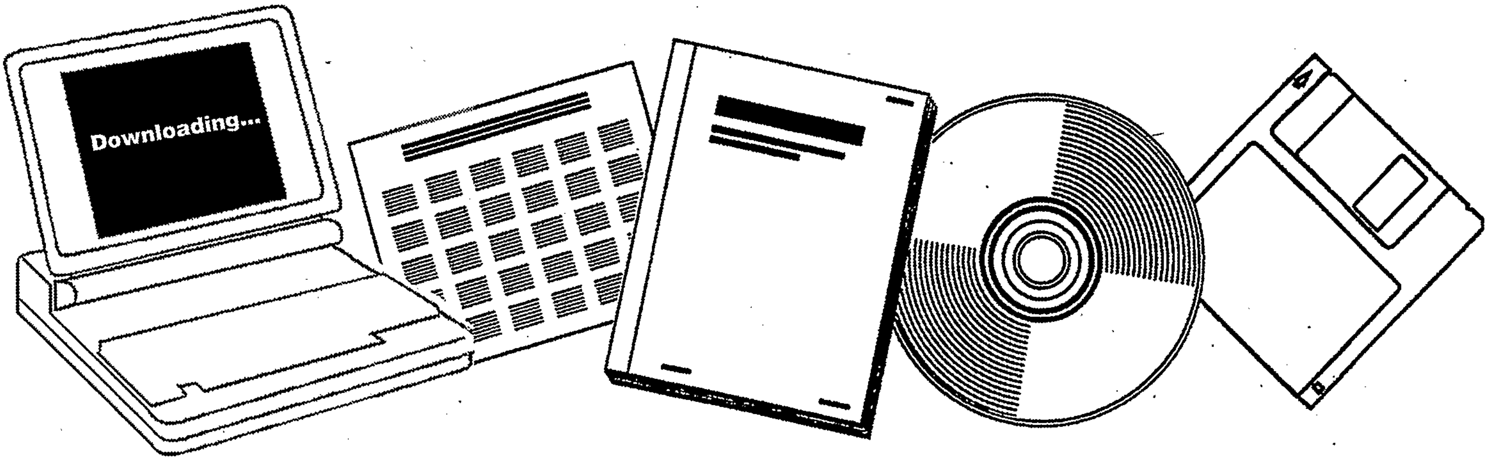

TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

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Eight Quarterly Report for Period
June 1,1985 to August 31,1986.

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OBJECTIVES

Task 1. Preperation 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

The major thrust of this work in the last quarter was to study the effect of the reacting gas phase on the behaviour of the catalyst by infrared spectroscopy. Effects of composition of gas, pressure and temperature were investigated for promoted and non-promoted systems.The appearance and relative stability of linear, bridged and geminal dicarbonyl species of chemisorbed carbon monoxide was observed and is discussed. Strategies for detailed kinetic modelling are discussed. In addition, kinetic measurements were carried out on a molybdena promoted catalyst. The problem of identifying primary and secondary reactions and products for a complex reaction network is tackled.

Task 1 and 2: Catalyst preperation and testing for syngas conversion

Extensive testing was done for the system 3%Rh 7.5% Mo /Al_2O_3. The data is shown in table 1.

Task 3: Measurement of surface composition and structure

Infrared spectroscopy is a very valuable tool for determining the local environment around an atom in an oscillator. The problem is tackled in two stages using carbon monoxide as a probe molecule. Extensive low pressure work has been done on Rh/Alumina. In the first stage the effect of promotion of sodium and molybdena is investigated using the earlier work done on non-promoted system. In the second stage the effect of pressure will be investigated.

Earlier results of preliminary high pressure work was discussed previously(fifth quarterly report). These runs were made on 3%Rh/Al_2O_3 and 3%Rh2%Na/Al_2O_3 where large downshifts in the IR frequency of adsorbed linear and bridged CO species were observed in the sodium promoted system. Both the catalyst samples were used (around 48 hours of reaction time), then mixed with Degussa alumina and re-reduced at 200C. The TPD/TPR results in the previous quarterly report showed that re-reduction of used catalyst at 200C is sufficient for reducing the surface layer of oxidised Rhodium particle. The above problem of using used catalyst for high pressure infrared spectroscopy is because of the temperature limit on the sealing material used in the cell.

A series of low pressure experiments were done to investigate the following parameters for sodium and molybdena promoted Rhodium on Alumina.

1. Adsorptive behaviour of used catalyst as compared to adsorptive behaviour of fresh catalyst.
2. Temperature stability of various species on the surface of the catalyst.
3. Stability of different species as a function of partial pressure of CO.

No shifts in the frequency of linear CO and gem-dicarbonyl CO have been found for fresh sodium containing catalyst at room temperature and at 1 atm pressure. The catalyst was reduced at 400C.

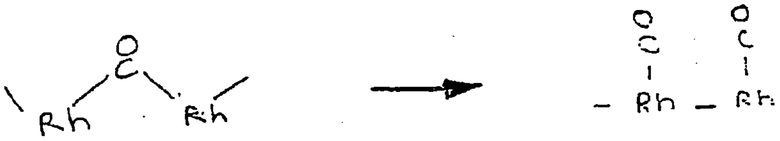
The conclusions reached from comparison of sodium promoted system with Rh/A1203 are:

1. In sodium promoted system at 30C the linear species is much more stable than in the non-promoted case at pressure of about 0.001 torr.

2. Linear species is stable at 50C for sodium promoted system, but this is not the case for unpromoted system (Figure 2).

3. Two other bands appearing at 1699 cm^{-1} and 1656 cm^{-1} are connected with the presence of sodium (probably formate species).

4. At 30C bridged species gets converted to linear species. This can be followed by observing the increasing absorbance of linear species.



$3\%Rh2\%Na/Al_2O_3$, 30C.

Time after starting evacuation	Absorbance[peak heights] linear	bridged
t=0 minute	0.1798	0.0905
t=10 minute	0.1922	0.0776

The bands at 1699 cm^{-1} and 1656 cm^{-1} increase with time; the reason behind this is not clear.

The higher stability of linear species in the sodium promoted catalyst can be explained as follows. In certain cases when carbon monoxide adsorbs on a surface of a rhodium metal crystallite it breaks up the crystallite. This can be explained in terms of usual bonding picture between CO and a transition metal. In this case the highest occupied molecular orbital of CO interacts with the metal atom while the metal donates electrons from its d orbitals to the lowest unoccupied molecular orbital which weakens the C-O bond. The same d orbitals of metal are responsible for metal-metal bonds in a crystallite.

When CO is adsorbed on a metal crystallite, electrons are partially withdrawn from the orbitals which are responsible for metal-metal bonds in a crystallite. This weakens the crystallite and in some cases it breaks it up. It is facilitated by surface OH groups(1). The formation of geminal dicarbonyl species from linear and bridged species is an evidence of this phenomenon.

However there is a critical size (or a critical reduction temperature since particle size is dependant on the reduction temperature) above which the metal particle holds together. This is because the ratio of number of Rh atoms on the surface to the Rh atoms in the bulk is so small that the effect of backbonding is minimized.

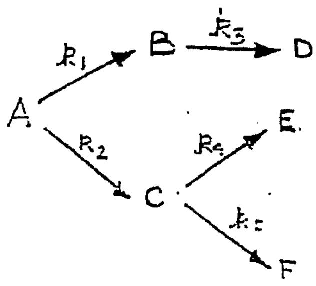
Whenever a Rh atom on the surface of a crystallite is blocked, it causes less backbonding, which in turn increases the stability of the crystallite. In sodium promoted system, sodium ion and its co-ion occupies a substantial part of the crystallite surface, this gives rise to increased stability of the linear species. A similiar effect is seen for used catalyst which has carbon deposited on its surface.

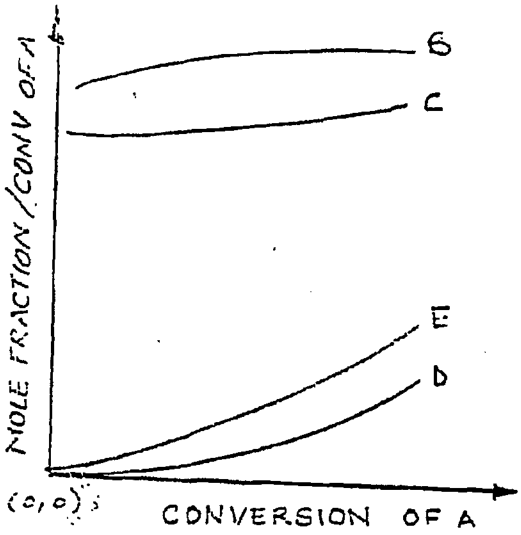
Task 4: Reaction mechanism determination by isotopic tracers and kinetics

Basic background procedures using direct integral method of kinetics is underway(2). Recent approaches using spline smoothing of data for better rate coefficient determination are also under investigation(3). The problem of identifying primary and secondary products and their regimes has been investigated in this quarter.

In a reaction network scheme if one plots [(molefraction of product)/(conversion of reactant)] against conversion of reactant, then one finds that the primary product have definite y-intercepts while the secondary products have zero intercepts. The value of the intercept is the ratio of the pseudo first order rate constant of the reaction leading to the formation of the product to the sum of all rate constants of the reactions where the reactant is consumed. Since the plots need not be straight lines, finding intercepts accurately is a problem. In case of sodium promoted Rh/Al2O3 the sum of the intercepts is around 0.9

e.g. for a scheme





y-intercept of B = $k_1/(k_1+k_2)$

y-intercept of C = $k_2/(k_1+k_2)$

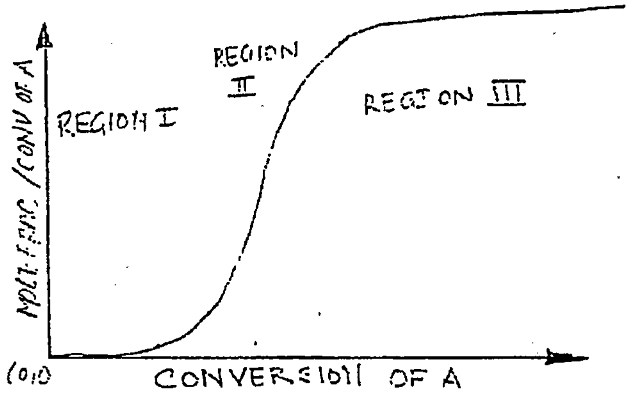
Kinetic schemes in CO hydrogenation catalysis have always been expressed by power law. The best work to-date is by Vannice where he investigates the power law kinetics of different supported noble metals(4). In his work he has dealt with hydrocarbon formation only. In promoted Rhodium system we have three main kinetic networks:

1. Methanol formation
2. Hydrocarbon formation
3. Higher Oxygenates formation

and three other reactions ether formation, ester formation and water gas shift reaction. By changing the relative importance of the schemes above we can get a broad range of product distribution. The neccessary kinetic parameters must be identified and should be related to the catalyst composition, structure and the chemistry of the reactions involved. The dependance of pseudo first order rate constants on partial pressure of reactants are investigated for molybdena promoted catalyst and are reported in Table 1. The data reported in table 1 is for low conversions, future experiments would encompass higher conversions. However the assumption of neglecting the effect of water on gas chromatograph data analysis would break down at higher conversions. The data at extremely low conversion shows considerable scatter at the same GHSV, because the error in sample analysis becomes substantial.

A brief summary for sodium promoted system is given below(see figures 4,5,6 and 7)

1. As expected MeOH and methane are primary products, the y-intercepts of MeOH is approximately .05 while the y-intercept of methane is approximately 0.46, this shows how methane pathway is so predominant over the MeOH pathway.
2. Ethane is a secondary product, hence either one of the following steps is unidirectional
    - a. CH_x insertion
    - b. C_2H_x hydrogenation
    - c. C_2H_6 desorption
3. AcOH, MeCHO and EtOH are primary products. This indicates that CO insertion and subsiquient hydrogenation of the CH_x precursor is very fast.
4. The decreasing slope of CO_2 makes it difficult to say whether CO_2 is a primary or secondary product.
5. Figure 5 shows that AcOH and MeOAc follow extremely closely which indicates that the formation of ester is very fast and is limited by formation of AcOH(or of acetyl species on the surface).
6. EtOAc has a s-shaped curve which indicates that the pathway is of the following type.



$$A \xrightarrow{I} B \overset{II}{\rightleftharpoons} C$$

In region I, the step II falls out of equilibrium because the contact time is so low. An order of magnitude estimate of the lowest rate constant in the composite step II can be easily estimated.

pseudo first order rate constant=

= O(13 sec-1)

7. Overall rate constant for sodium promoted system is 0.013 sec-1 at 250c , CO/H_2=1:2 and at 450psig(figure 8). Figure 9 and 10 show the effect of partial pressure on the overall rate constant for molybdena promoted system.

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3. Vajda S., Valko P. and Yermakova A.,Computers and Chemical Engineering, 10(1), 49(1986)
4. Vannice M.A., in "Catalysis:Science and Technology", volume 3, Springer Verlag, 1982.

Table 1:

mo75dk july 16.1986.   3%Rh 7.5% Mo/Al2O3, 200C

P.P. CO	P.P. H2	P.P. He	GHSV hr-1	time hrs	%COconv incl CO2	time @ condition	MOLE FRAC CONV CO
150	300	0	5984	12	2.5	12	3.97E+01
150	300	0	5984	14	2.8	14	3.54E+01
150	300	0	5984	15	2.6	15	3.78E+01
150	300	0	5984	16	2.6	16	3.71E+01
150	300	0	2992	19	5.6	3	1.72E+01
150	300	0	2992	20	5.8	4	1.66E+01
150	300	0	2992	21	6.1	5	1.57E+01
150	300	0	8976	22	1.8	1	5.59E+01
150	300	0	8976	23	1.5	2	6.64E+01
150	300	0	8976	24	1.8	3	5.51E+01
150	300	0	10472	33	1.4	9	7.01E+01
150	300	0	10472	34	1.3	10	7.49E+01
150	300	0	10472	36	1.2	12	8.07E+01
150	300	0	11968	37	1.1	1	8.79E+01
150	300	0	11968	38	1.0	2	9.94E+01
150	300	0	11968	39	1.1	3	9.44E-01
150	300	0	13464	41	0.7	1	1.44E+02
150	300	0	13464	42	0.9	2	1.11E+02
					0		
75	150	225	2992	13	4.8	13	2.03E+01
75	150	225	2992	14	4.5	14	2.16E+01
75	150	225	2992	16	4.2	16	2.30E+01
75	150	225	4488	17	2.3	1	4.22E+01
75	150	225	4488	18	2.6	2	3.75E+01
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.5	1	5.50E+01
75	150	225	5984	20	1.6	2	6.25E+01
75	150	225	5984	21	1.4	3	7.15E+01
75	150	225	8976	32	0.9	3	1.15E+02
					0		
80.35714	160.7142	208.9285	7480	22	1.0	1	1.03E+02
80.35714	160.7142	208.9285	7480	35	0.9	14	1.14E+02

Table 1(cOntd):

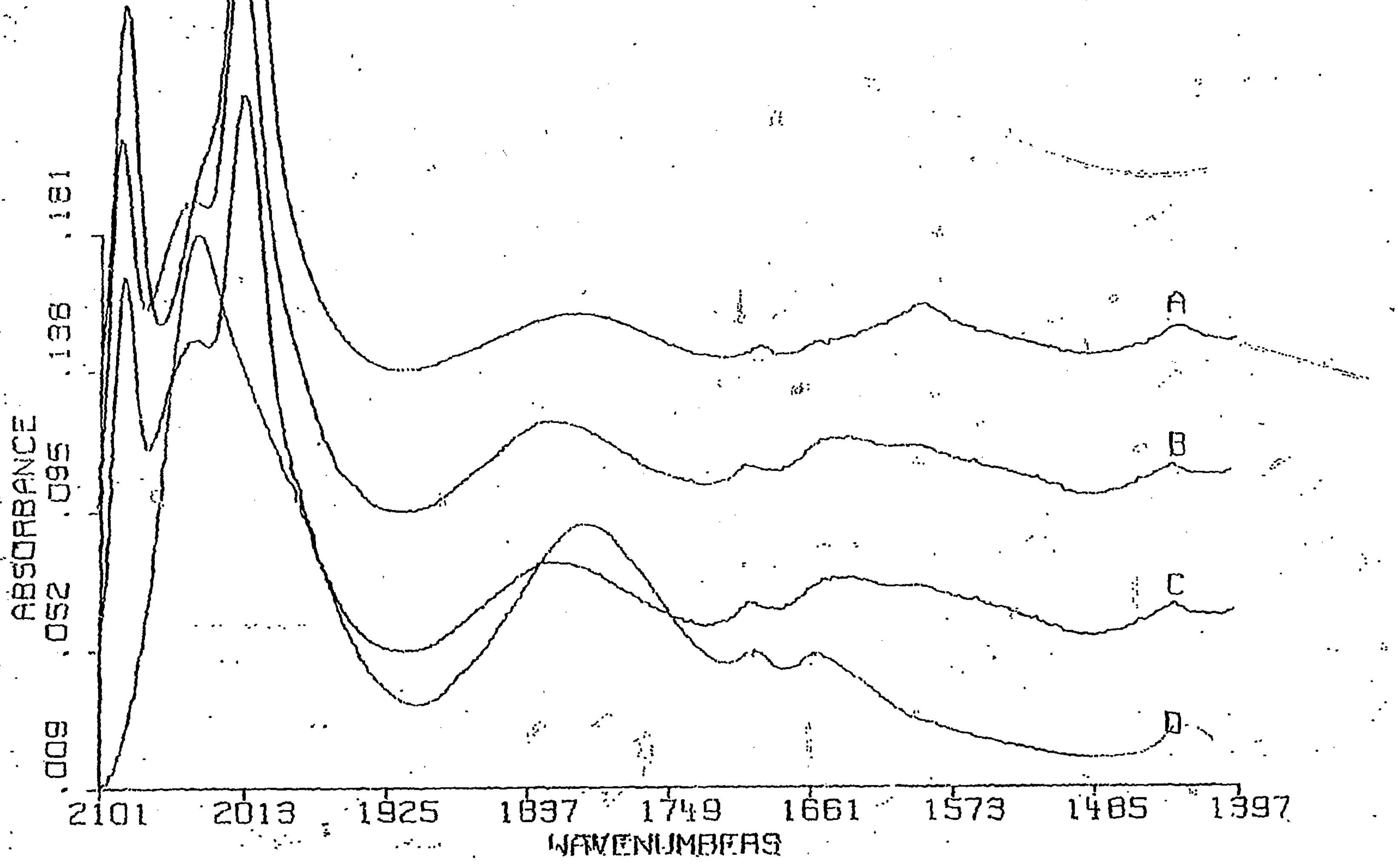
mo75dk july 16,1986.

MOLE FRACTION/CONVERSION OF CO.

CH4	CO2	C2H6	MeOH	MeOMe	EtOH	MeOEt	MeOAc
1.35E-02	0.2422	0	0.3210	0.1409	0.02998	0.02902	0.00000
4.97E-02	0.2072	0	0.2549	0.1880	0.02483	0.02323	0.00000
4.32E-02	0.2242	0	0.2682	0.1617	0.03149	0.02815	0.00000
3.97E-02	0.2177	0	0.2586	0.1741	0.03006	0.02757	0.00000
6.99E-02	0.2704	0.011315	0.2091	0.1520	0.02488	0.02650	0.00284
6.56E-02	0.2631	0.003204	0.1988	0.1645	0.02511	0.02601	0.00798
4.90E-02	0.2552	0.007653	0.1907	0.1684	0.02973	0.02486	0.01198
3.62E-02	0.1881	0	0.2545	0.1960	0.02761	0.02629	0.00000
4.39E-02	0.1964	0	0.2925	0.1666	0.02847	0.02686	0.00000
3.60E-02	0.1579	0	0.2589	0.2118	0.02781	0.02435	0.00000
4.01E-02	0.1580	0	0.2687	0.1797	0.03677	0.03480	0.00000
4.27E-02	0.1673	0	0.2850	0.1953	0.02406	0.02319	0.00000
4.55E-02	0.1742	0	0.3053	0.1789	0.02198	0.02541	0.00000
4.05E-02	0.1497	0	0.2762	0.2251	0.01340	0.01989	0.00000
4.56E-02	0.1684	0	0.3035	0.2022	0.01508	0.01679	0.00000
2.92E-02	0.1629	0	0.3047	0.2183	0.01449	0.01344	0.00000
3.95E-02	0.1596	0	0.3454	0.1935	0.01087	0.01614	0.00000
3.02E-02	0.1376	0	0.3011	0.2383	0.00998	0.01234	0.00000
0	0	0	0	0	0	0	0
8.33E-02	0.2423	0.013625	0.1399	0.1786	0.01667	0.03962	0.00000
8.64E-02	0.2545	0.018332	0.1422	0.1598	0.02241	0.04290	0.00000
1.18E-01	0.2517	0.017014	0.1586	0.1482	0.01533	0.04044	0.00000
1.76E-02	0.2551	0.019049	0.1965	0.1611	0.02151	0.04538	0.00000
9.96E-02	0.2186	0	0.1769	0.1630	0.00855	0.05643	0.00000
1.72E-02	0.2139	0	0.2100	0.2127	0.00000	0.04635	0.00000
2.73E-02	0.2036	0	0.1266	0.1976	0.02420	0.06823	0.00000
3.30E-02	0.2393	0	0.2065	0.1786	0.00000	0.05598	0.00000
5.65E-02	0.1922	0	0.1373	0.2346	0.00000	0.04920	0.00000
0	0	0	0	0	0	0	0
6.83E-02	0.2194	0	0.2194	0.1147	0.00000	0.08951	0.00000
6.85E-02	0.2487	0	0.2616	0.1214	0.00000	0.06014	0.00000

FIGURE 1
3%RH 2%NA/AL2O3:REDUCED AT 400C
EXPOSED TO CO AND EVACUATED
A-100C:B-75C:C-50C:D-30C

NOTE:Y-AXIS SCALE IS ONLY FOR SPECTRUM D



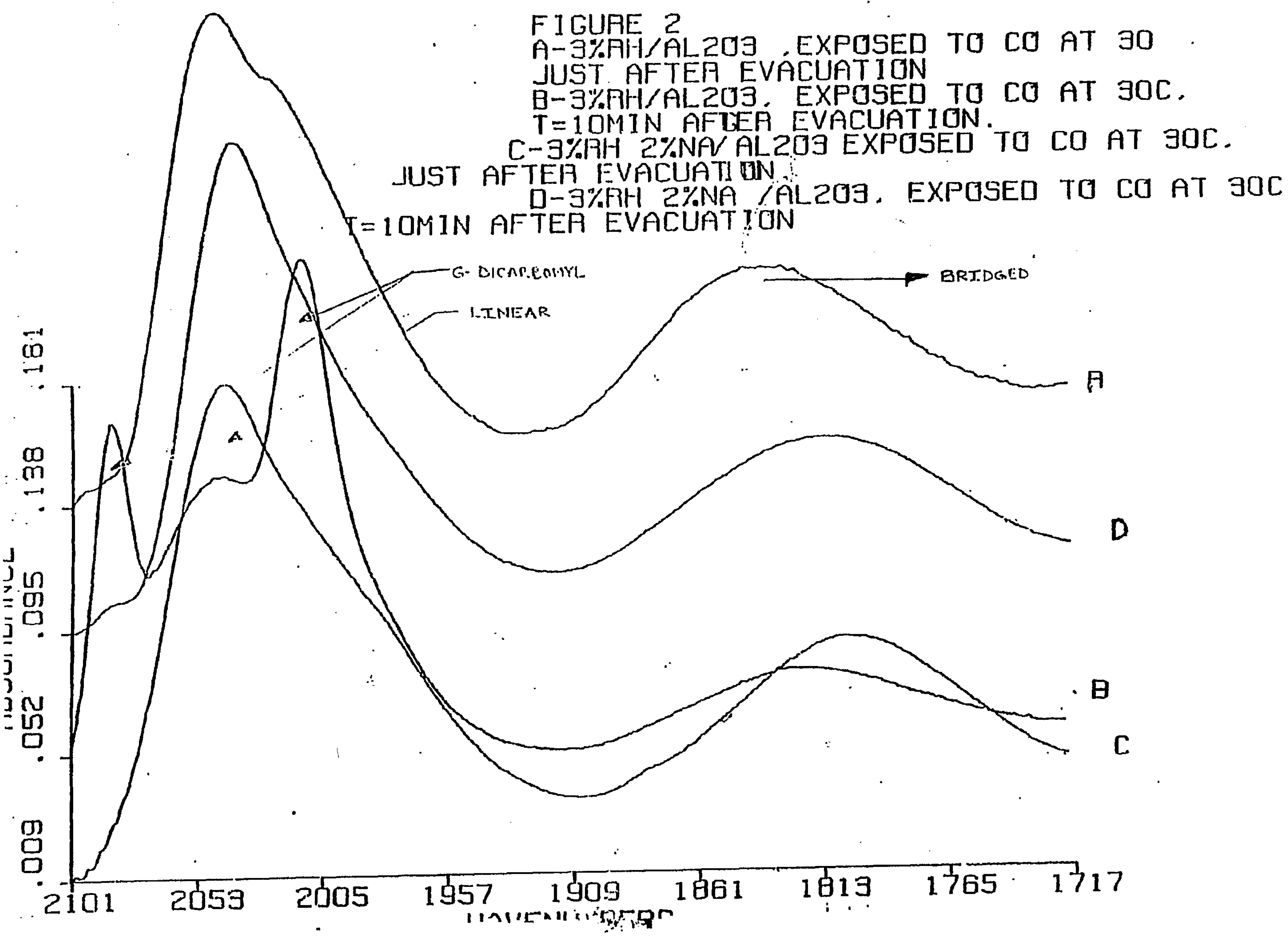


FIGURE 2
A-3%RH/AL203 ,EXPOSED TO CO AT 30
JUST AFTER EVACUATION
B-3%RH/AL203, EXPOSED TO CO AT 30C,
T=10MIN AFTER EVACUATION.
C-3%RH 2%NA/AL203 EXPOSED TO CO AT 30C.
JUST AFTER EVACUATION.
D-3%RH 2%NA /AL203, EXPOSED TO CO AT 30C
T=10MIN AFTER EVACUATION

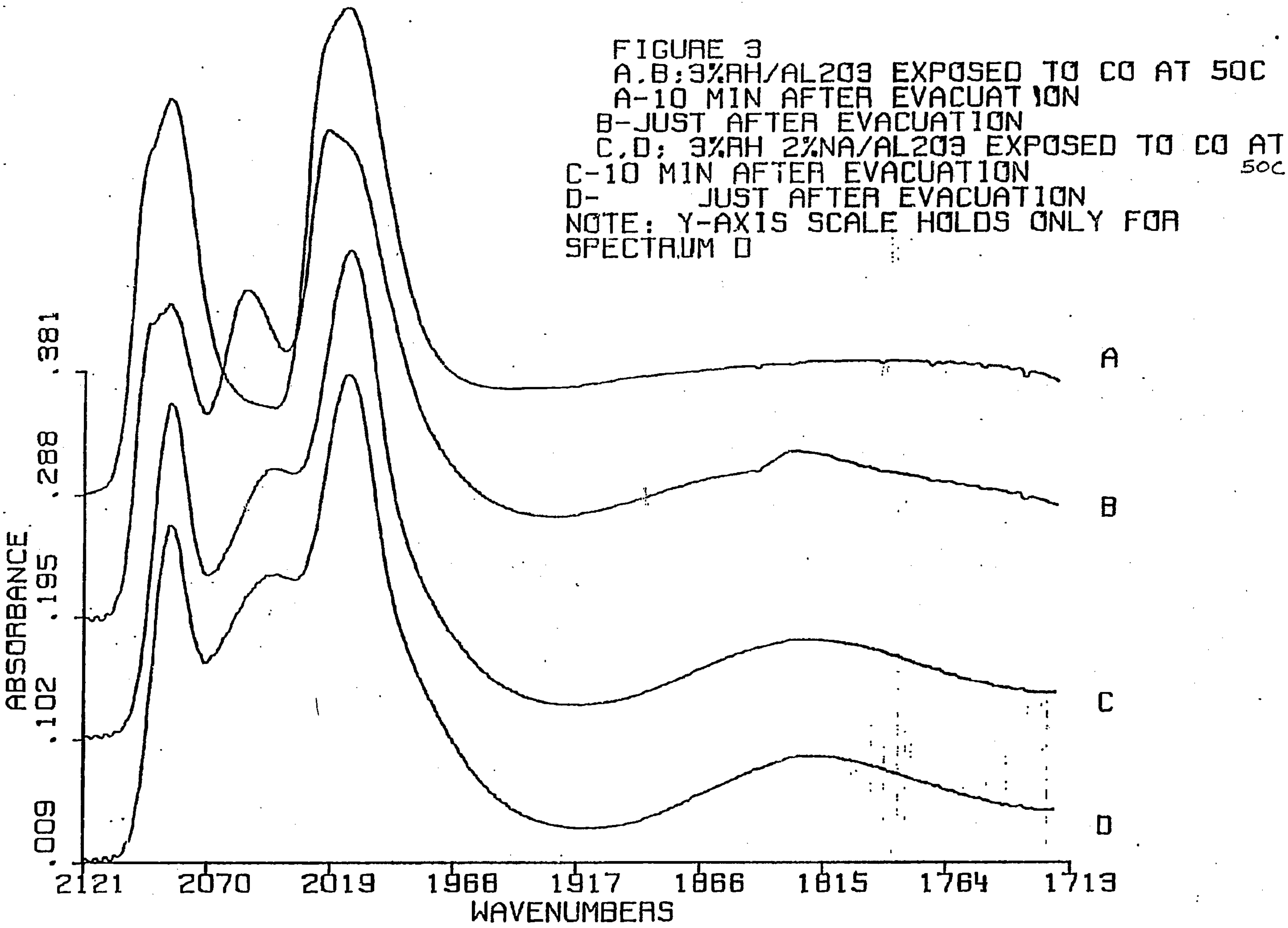


FIGURE 3

A.B:3%RH/AL2O3 EXPOSED TO CO AT 50C

A-10 MIN AFTER EVACUATION

B-JUST AFTER EVACUATION

C.D: 3%RH 2%NA/AL2O3 EXPOSED TO CO AT 50C

C-10 MIN AFTER EVACUATION

D- JUST AFTER EVACUATION

NOTE: Y-AXIS SCALE HOLDS ONLY FOR SPECTRUM D

Figure 4: EFFECT OF SECONDARY REACTIONS

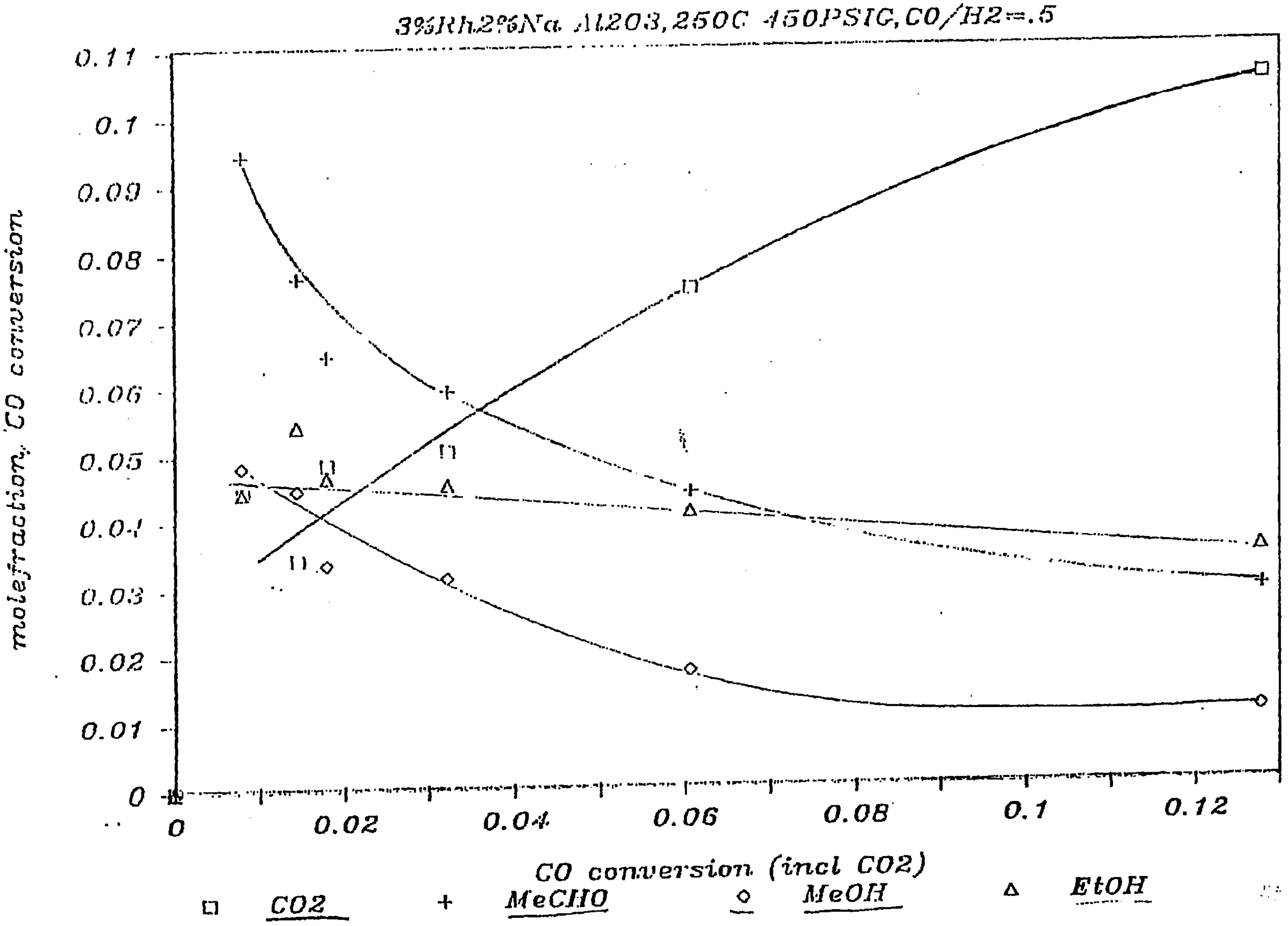
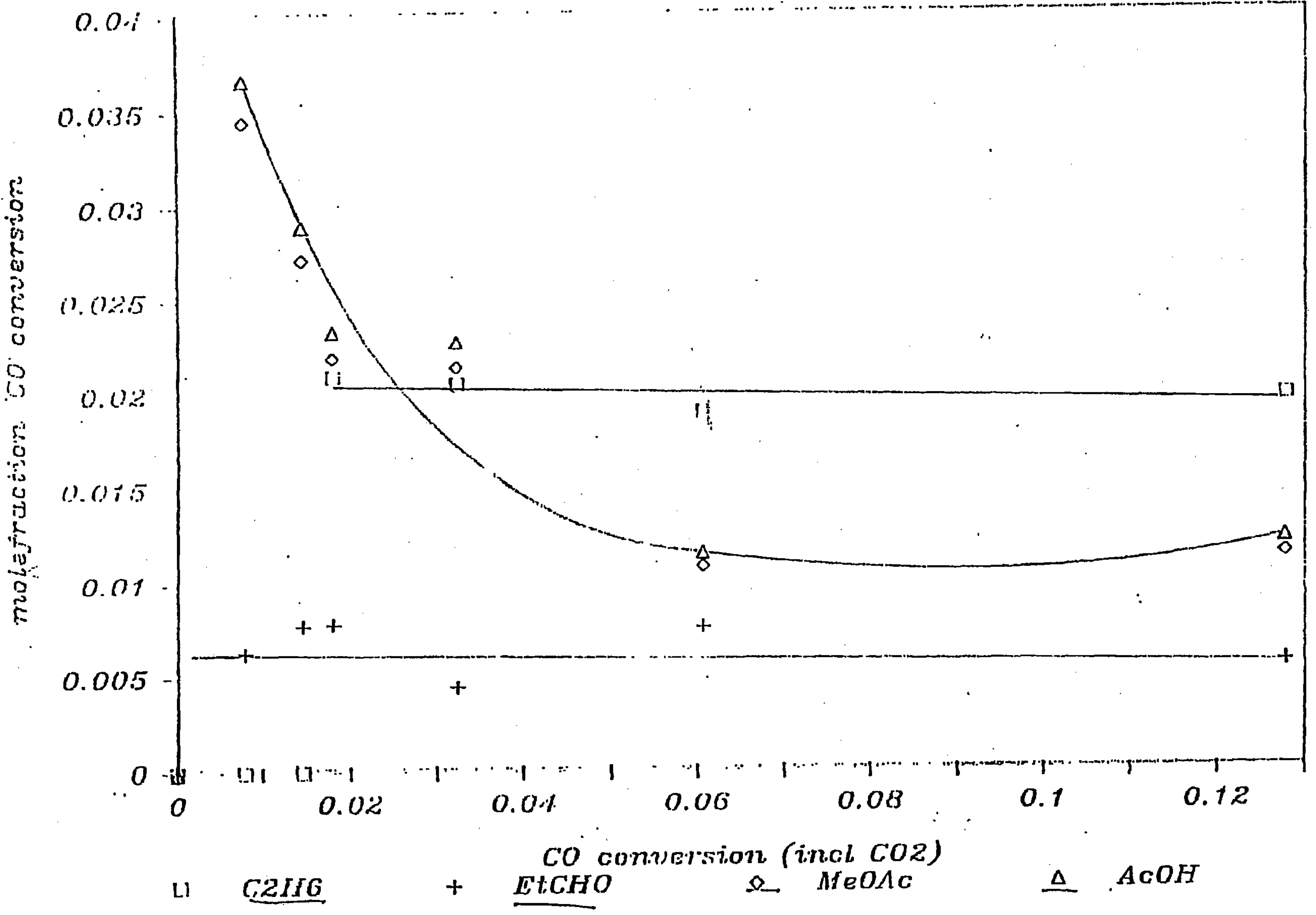


Figure 5:



EFFECT OF SECONDARY REACTIONS

3%Rh2%Na Al2O3,250C 450PSIG,CO/H2=.5

Figure 6:

EFFECT OF SECONDARY REACTIONS

3%Rh2%Na Al2O3,250C 450PSIG,CO/H2=.5

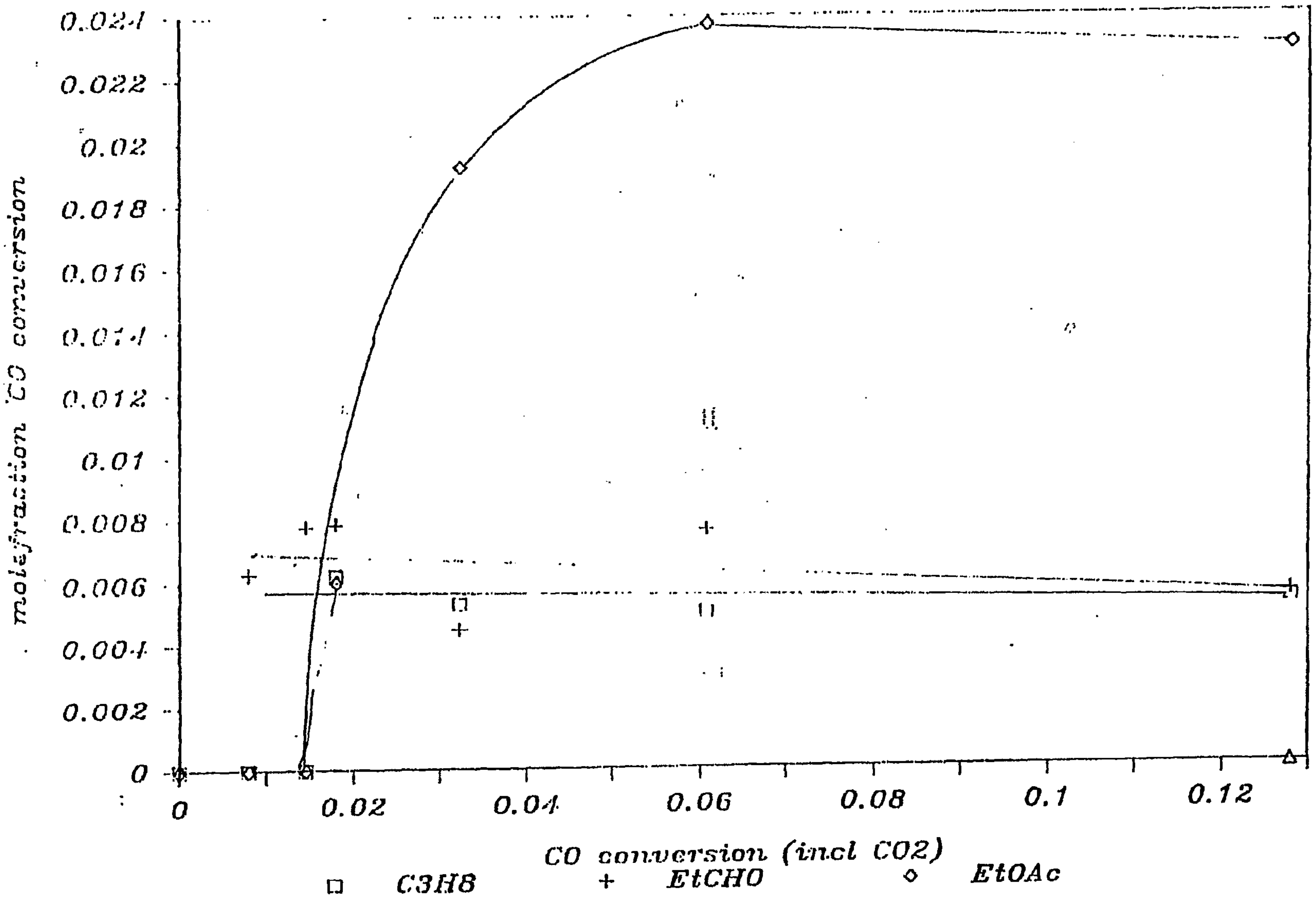


Figure 7: EFFECT OF SECONDARY REACTIONS

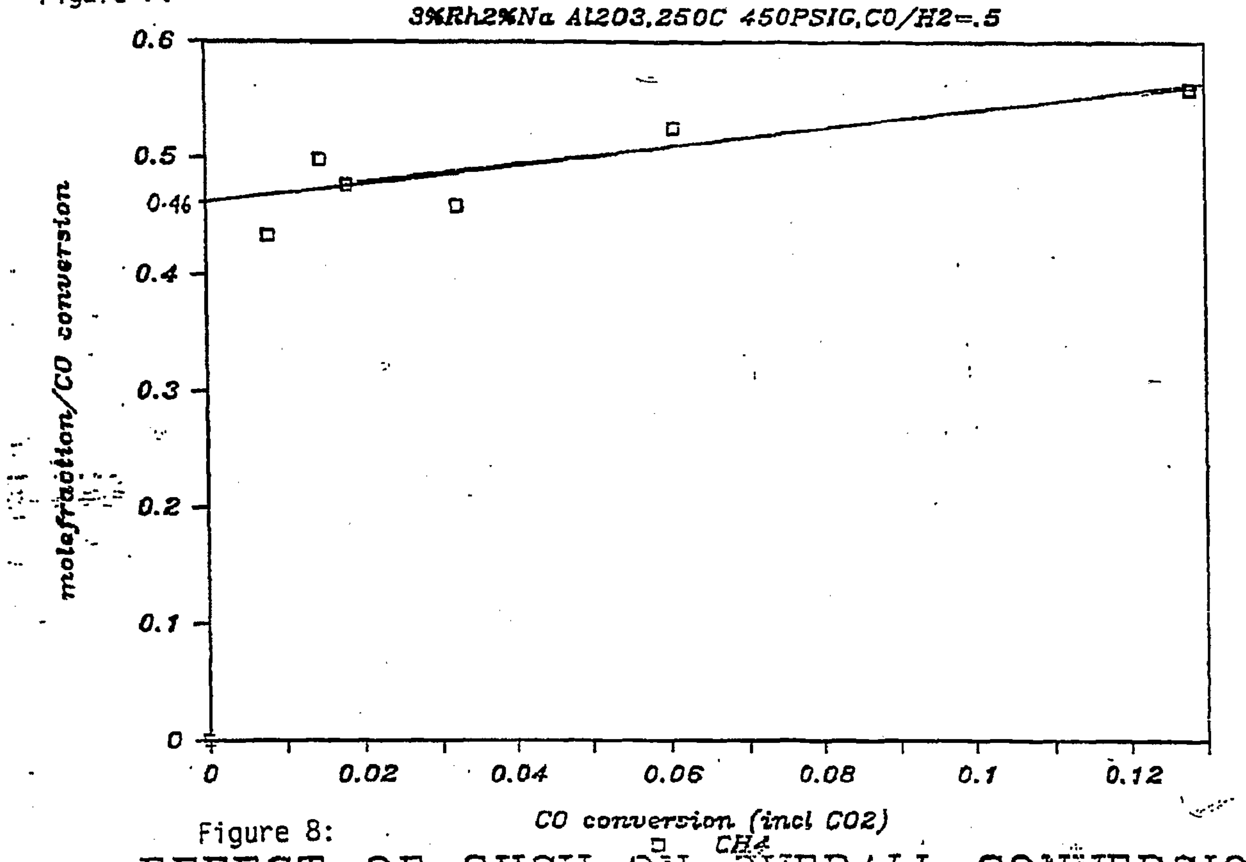
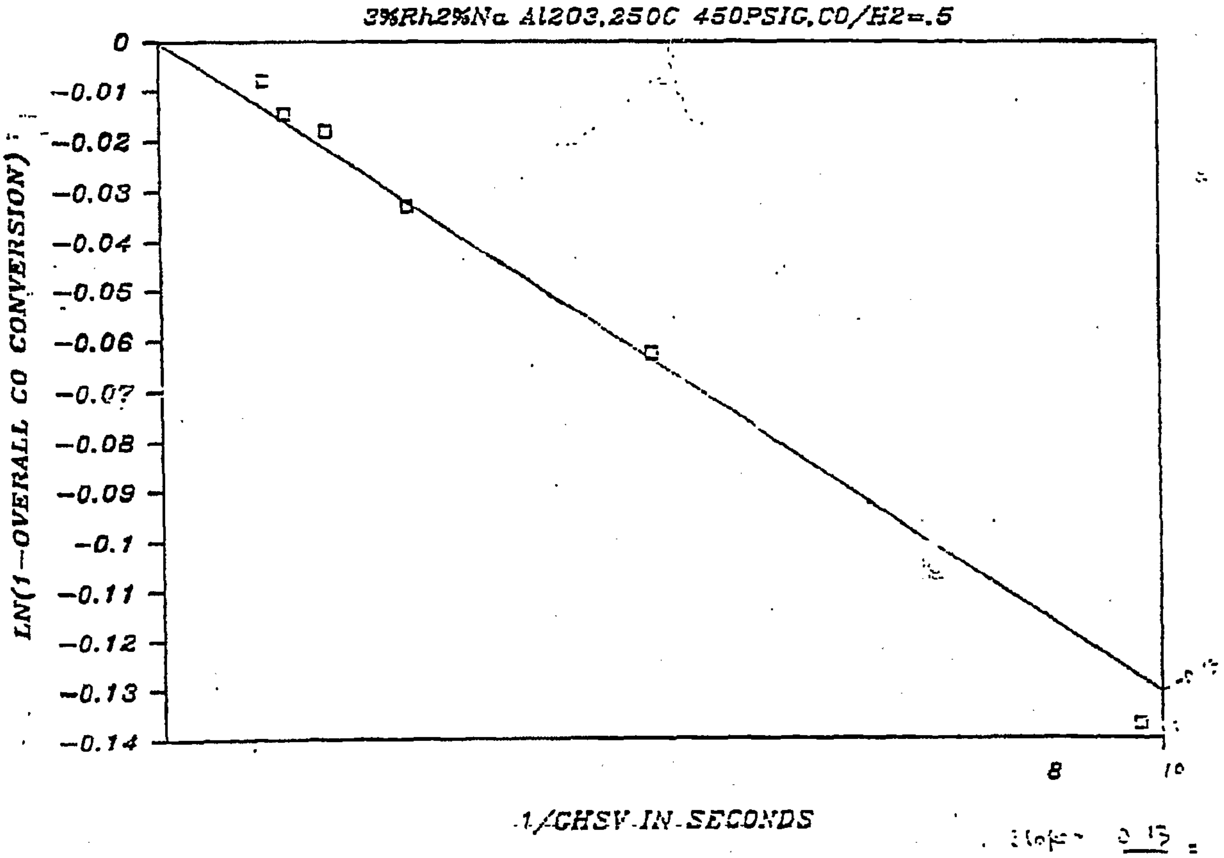


Figure 8: EFFECT OF GHSV ON OVERALL CONVERSION



Slope = $\frac{0.13}{10}$ = 0.013 s

= 0.78 mi

Figure 9:

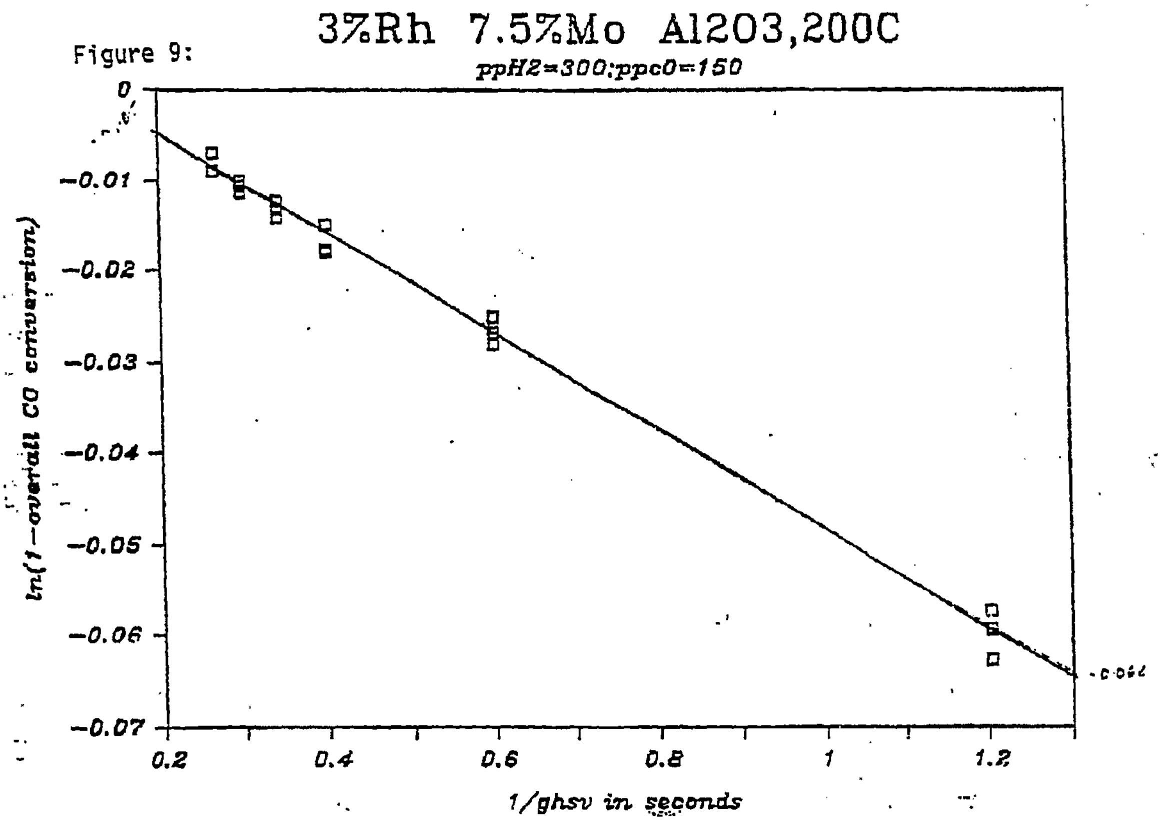


Figure 10: