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TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS. FIFTH QUARTERLY REPORT, SEPTEMBER 1-NOVEMBER 30, 1985

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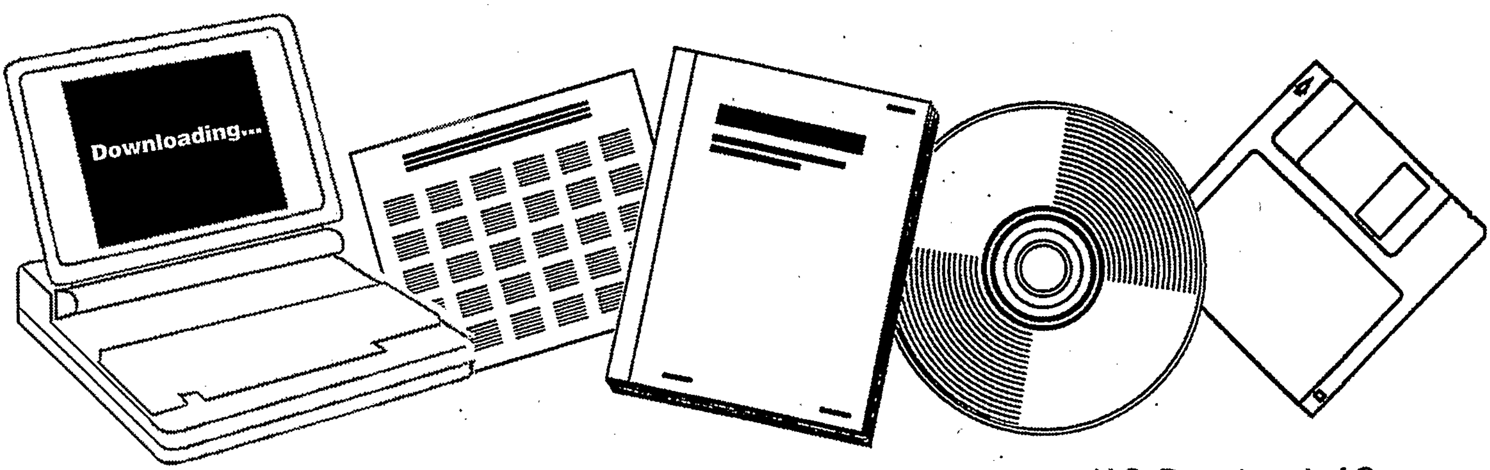

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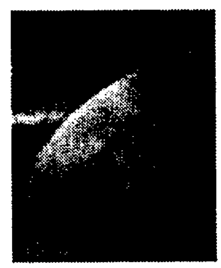

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TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

Fifth Quarterly Report for Period
September 1, 1985 to November 30, 1985

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MASTER

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OBJECTIVES

ık 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

The identification and analysis of all the individual reaction products formed in the CO hydrogenation over rhodium catalysts has been achieved. This has not been reported by previous workers. The reaction products contain significant amounts of all five classes of oxygenates (namely alcohols, aldehydes, acids, esters and ethers), C1 to C5 hydrocarbons, in addition to carbon dioxide and water formed by the shift reaction.

In a series of tests using a Na-Rh/alumina catalyst,varying space rate was used to vary CO conversion from 1 to 13%. Selectivity to oxygenates decreased with increasing conversion. Over this range the C2 oxygenates were found to be a remarkable ca 80% of all oxygenates. From a plot of production of C2 oxygenates as a function of CO conversion, the build-up of secondary reaction products can be observed, which indicates, for example, the sequential formation of acetaldehyde, hydrogenation to ethanol and, with acetic acid, conversion to ethyl acetate.

Six new catalysts were prepared to test out various ideas.
- Ce addition to Rh/alumina increased selectivity to oxygenates slightly.
- Sn addition to Rh/alumina caused essentially complete deactivation.
- Rh deposited on alumina as the unusual rhodium acetate dimer was not active at low temperature as hoped. Also at higher temperatures where the complex decomposed, the selectivity to oxygenates was poor.
- Na added to <u>prereduced</u> Rh/alumina performed identically to a catalyst in which Na and Rh were <u>codeposited</u> on alumina.
- Rh deposited on alumina from Rh trichloride solution gave the same results as catalyst prepared using Rh trinitrate solution.

Progress was made in catalyst characterization using chemisorption, infrared measurements and temperature programmed desorption.

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

This report provides for the first time detailed analyses of individual products distributions for each of the hydrocarbons and oxygenated compounds. This information appears in Tables I and II which are produced using the new computerized system. In these :

- the basis for C2+ oxygenates is % of total oxygenates on a carbon dioxide-free basis.
- propane/methanol are found in as single peak and acetic acid/ methyl acetate in another peak. Their separate values have been eestimated.
- the butane/methyl ethyl ether peak has now been resolved by preparation of the ether and using it to calibrate the GC system.

Table I lists new catalyst preparations.

4% Ce,3% Rh/Alumina catalyst is slightly less active than standard Rh/Alumina, but has somewhat improved selectivity to oxygenates production, Fig. 1.

3.6% Sn,3% Rh/Alumina catalyst was prepared to test the idea that tin would improve the selectivity of the Rh/Alumina. However, this catalyst proved to be inactive.

1% Rh/Alumina catalyst, was prepared using rhodium acetate dimer. The $Rh_2(OOCCH_3)_4$, first synthesized in 1962 is an unusual Rh^{II} compound which has a strong rhodium-rhodium bond. It has previously been found to be active as a catalyst for hydrogenating olefins. The concept was that this compound, anchored on alumina, would have unusual catalytic properties because of its Rh-Rh bond. Worley et al., J.Chem. Phys. 76,No 1, (1982), found by infrared spectroscopy that, when deposited on alumina, the dimer structure was retained at 150°C but not 400°C. However as seen in Table I, the catalyst prepared from the dimer was not active until about 225°C and above where it is believed that the complex decomposes. Furthermore, the selectivity was distinctly poorer than the standard Rh/Alumina pepared from rhodium nitrate, Fig. 1.

1% Na, 3% Rh/Alumina catalyst was prepared with sodium added as NaOH to a <u>prereduced</u> Rh/Alumina to test the idea that the sodium would act differently than when <u>codeposited</u> with the rhodium. The activity,Table I, and the selectivity, Fig. 1, were the same as with catalysts prepared by codeposition. The catalyst has about 1/4 the activity of Rh/Alumina without sodium.

3% Rh/Alumina catalyst was a fresh preparation from $Rh(NO_3)_3$ solution. It was used to evaluate reproducibility and to provide data to settle the butane/methyl ethyl ether analytical question. Activity and selectivity data confirm previous results for this type of catalyst.

3% Rh/Alumina catalyst was prepared from $RhCl_3$solution to evaluate whether chloride remaining on the alumina after reduction would impart extra acidity which would affect catalyst performance,This catalyst was essentially identical to the standard Rh/Alumina, Fig. I.

Table II provides detailed product analyses for catalysts previously reported in less detail. Interesting variations in product distributions are observed and have not previously been reported by others. The significance of these is being analyzed. Some inferences on reaction mechanisms are given later under Task 5.

Task 3 and 4: Determination of Surface Composition, Stucture and Complexes.
INFRARED .Some changes have been made in the infared cell which have led to higher operating pressure. These changes include
(A) redesign of spacer rings.
(B))repolishing of contact surfaces
At present the cell can withstand pressures up to 600 psi at 200°C .It is being modified to extend it to 1,000 psi.
Other modifications have been made on the 'cart' due to failure of some components.
(i) two needle valves have replaced a back pressure regulator.
(ii) the valve vmm#3 (Fig.3) has been replaced and now it is out of mixing manifold.
(iii) the high temperature/high pressure GC sampling valve has been removed temporarily.
(iv) since CO_2 was being produced in the CuO trap in the CO-module , the trap and the subsequent molecular sieve trap have been bypassed.
(v) Heating the mixing manifold was discontinued after it was found that no substantial amount of carbonyls were formed as long as gas was flowing through the mixing manifold.

(vi)An external CO-detector has been interlocked with the safety system on the cart.

A preliminary infrared pattern is shown in Fig. 3 for CO on Rh/Alumina which displays both linear and bridged structures but not g-dicarbonyl at higher tempeŕatures.

CHEMISORPTION. Hydrogen chemisorption values are now being determined. A dispersion of 35% was determined for a standard 3% Rh/alumina.

TEMPERATURE PROGRAMMED REDUCTION has been carried out and will be reported later as well as ESCA tests which will be started shortly.

Task 5 Determination of Reaction Mechanism.
One series of six experiments was carried out on a single 2%-Na,3% Rh/Alumina catalyst at constant conditions except for changing space rate. CO conversions varied from 0.8 tO 12.8 %. The variation in C2 oxygenates, summarized in table III, provides very interesting insight into the reactions which occur. Selectivity to total oxygenates decreases from 33 to 55 % over this conversion range.The C2 oxygenates as a percentage of total oxygenates is remarkably high, 87-79%. This is an interesting way of making C2 oxygenates, apparently not subject to the A-S-F limitation for alcohols. Hydrogenation of the products would provide high selectivity to ethanol.

Hoowever,it is recognized that for these catalysts the selectivity to hydrocarbons is high, selectivity for methane being 55-67%.

Fig 4 Shows a plot of selectivity vs conversion. Of more interest is Fig 5, where productivity (selectivity times conversion) is plotted vs conversion. Several interesting observations are apparent, especially relating to the secondary reaction products, which indicate the sequential formation of acetaldehyde, hydrogenation to ethanol and,with acetic acid, esterification to ethyl acetate.The amounts of ethyl acetate are remarkably high.

A detailed examination of product distributions reveals that addition of alkali to Rh/alumina deactivates hydrocarbon formation relatively more than that of oxygenates. Further, an important point is that while formation of C2+oxygenates decreases drastically, the formation of methanol remains almost unchanged. This selective change in selectivity is important in considering the chemical influence on reaction pathways, depicted in Fig. 6.

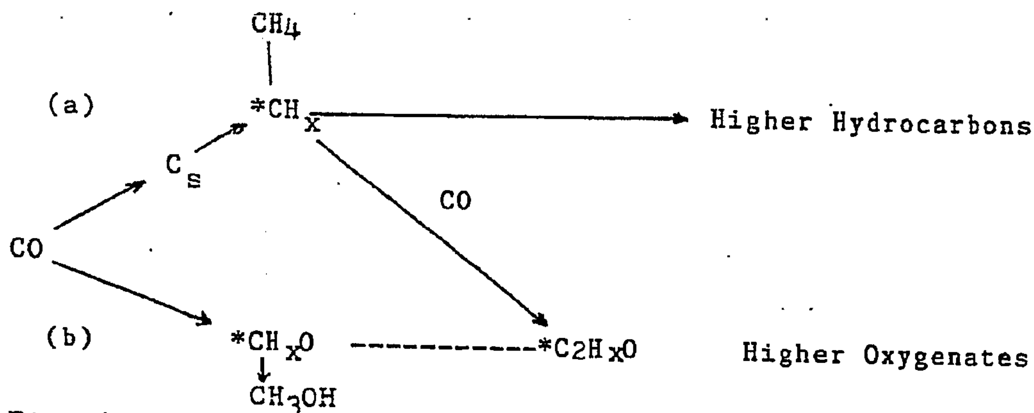


Fig. 6 Proposed reaction nework for CO hydrogenation.

To cause such a drastic change in catalytic properties, the alkali must interact with the surface rhodium in a special manner.
(a) Alkali may force Rh to form larger crystallites. This is precluded by the XRD results.
(b) Alkali rhodate may have formed which prevents reduction to Rh . XPS work is underway to test this hypothesis.
(c) Our view is that the Na alters the essential chemical nature of the catalytic site so as to interfere with activation of either of both H_2 and CO. In terms of a proposed reaction network, Fig 6 [see Chuang, Goodwin and Wender, J.Catal.95,435 (1985)],the present data show that the active site leading to route (a) is particularily poisoned, reducing the rate of the steps which lead to chain growth necessary for the formation of higher alcohols.The findings by McClory and Gonzales, J.Catal. 89,392 (1984), that alkali greatly reduces hydrocarbon synthesis over Ru/silica is very pertinent. They conclude that there is an ensemble of Ru atoms necessary for CO hydrogenation and that a very small amount of alkali can 'block' a whole ensemble. In our case, since alkali decreases conversion, and also the production of C2+ oxygenates, but not the formation of methanol, and since it is known from previous workers that the formation of methanol from CO and H_2 does not require an ensemble of atoms, the conclusion of McClory and Gonzales seems applicable here too.

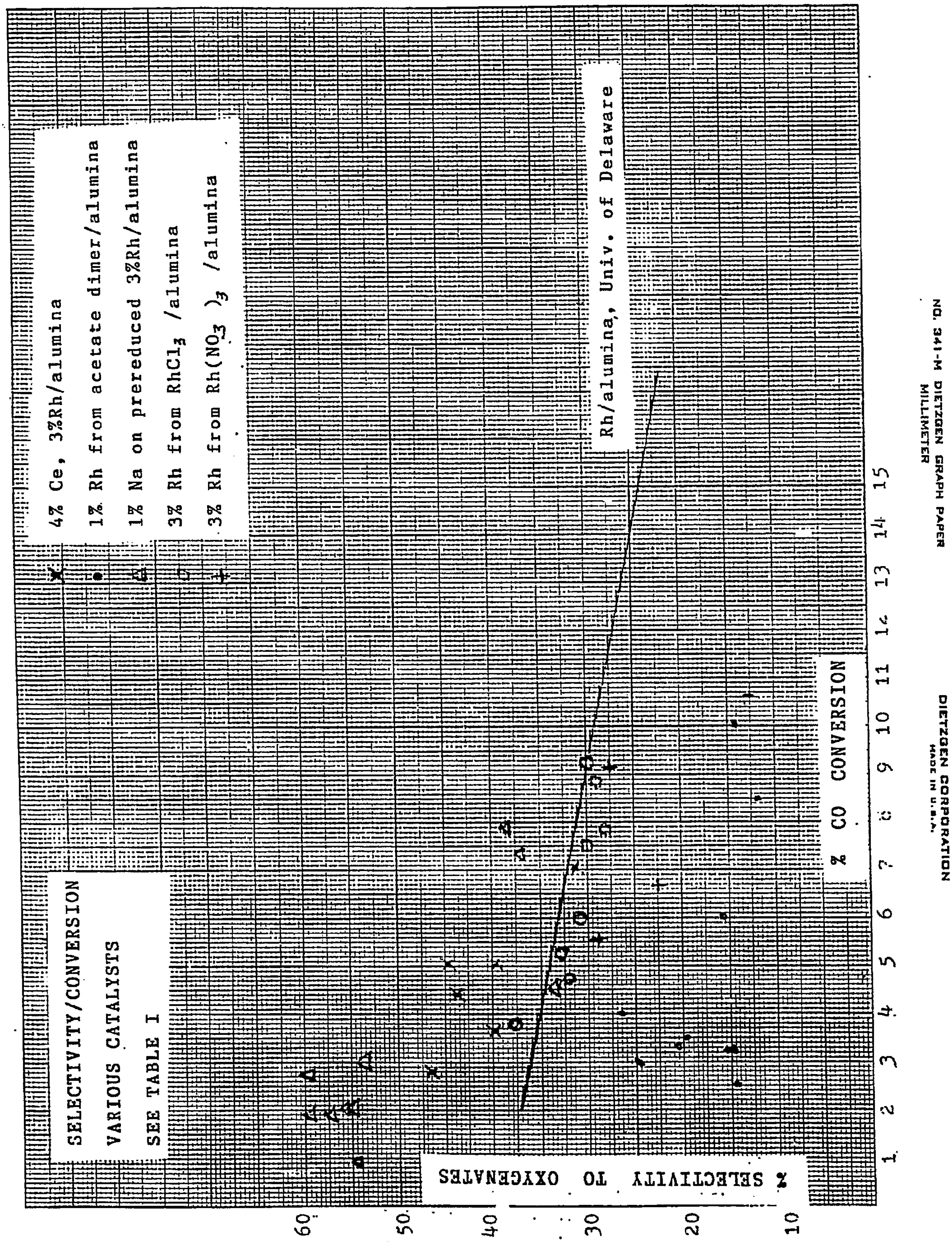
APPENDIX IDENTIFICATION OF UNKNOWN GC PEAK

It was mentioned in our previous quarterly reports that on alumina based rhodium catalysts, butane was apparently forming in amounts much larger than predicted by the Anderson- Shultz- Flory distribution. Later, from the time and temperature dependence of the GC peak (which had the retention time thought to be butane) it was suspected that this peak must consist of two products, namely butane and an oxygenate. It should be mentioned that the retention time did not match any of the previously reported oxygenates formed over rhodium catalysts. From the location of the peak from the Propak QS column, the oxygenate must have 2 or 3 carbon atoms, and a molecular weight slightly higher than that of ethanol. The only class of oxygenated products that other workers have not mentioned are ethers. The peak position is later than that of dimethyl ether and much earlier than that of diethyl ether. Therefore it was suspected to be methyl ethyl ether. This was confirmed with the preparation of an authentic sample prepared by reacting sodium ethoxide with methyl iodide in ethanol solution at 0° C and injecting it into the GC column.This particular oxygenate has not been reported by any previous workers for supported rhodium catalysts for syngas conversion. It should be noted that over rhodium/alumina catalysts methyl ethyl ether forms with considerable selectivity.

ANALYTICAL PRODUCTS IDENTIFICATION

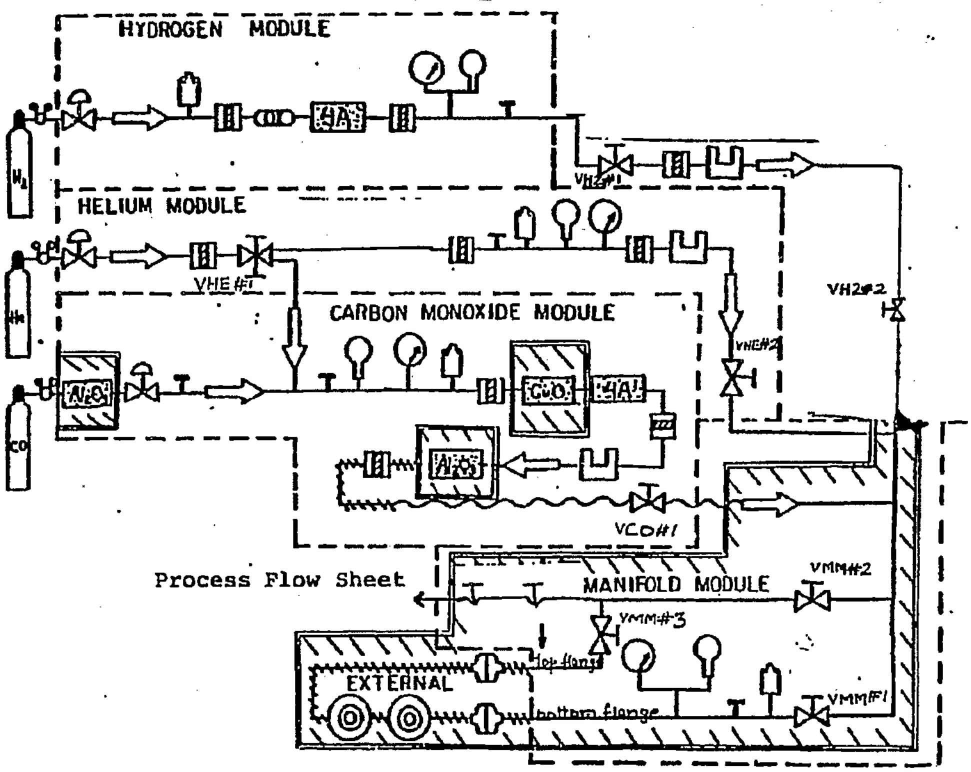
With the present analytical system (12 foot x 1/8 inch Poropak QS packed in teflon coated SS tubing) it is possible to separate and measure quantitatively most of the reaction products with three exceptions : (1) propane/methanol (2) butane/methyl ethyl ether and (3) methyl acetate/acetic acid. Each pair comes out as a different single peak. In order to provide a complete on-line analysis, we are planning to modify our analytical system by installing an available second gas chromatograph with a Poropak T column (7 feet x 1/8 inch). The manufacturers literature states that this column can carry out the required separations and we have already verified this. ~~for butane and methyl ethyl ether.~~ Simultaneous complete analysis will be possible by injecting reaction product mixture into two different columns, Poropak QS an T. It is believed that this will provide the most complete analytical system for analysis of products of CO hydrogention over rhodium catalysts which has been used by anyone.

FIG. 1



SELECTIVITY/CONVERSION
VARIOUS CATALYSTS
SEE TABLE I
4% Ce, 3%Rh/alumina
1% Rh from acetate dimer/alumina
1% Na on prereduced 3%Rh/alumina
3% Rh from RhCl3 /alumina
3% Rh from Rh(NO3)3 /alumina
Rh/alumina, Univ. of Delaware
% CO CONVERSION
% SELECTIVITY TO OXYGENATES
NO. 341-M DIETZGEN GRAPH PAPER
MILLIMETER
DIETZGEN CORPORATION

FIG. 2



Process Flow Sheet

Legend to Process Flow Sheet

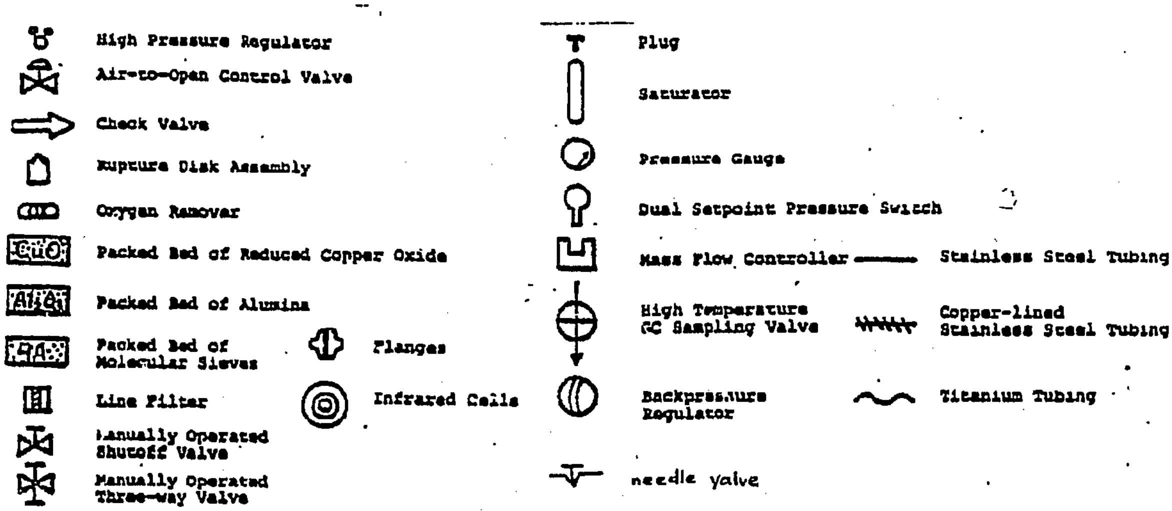
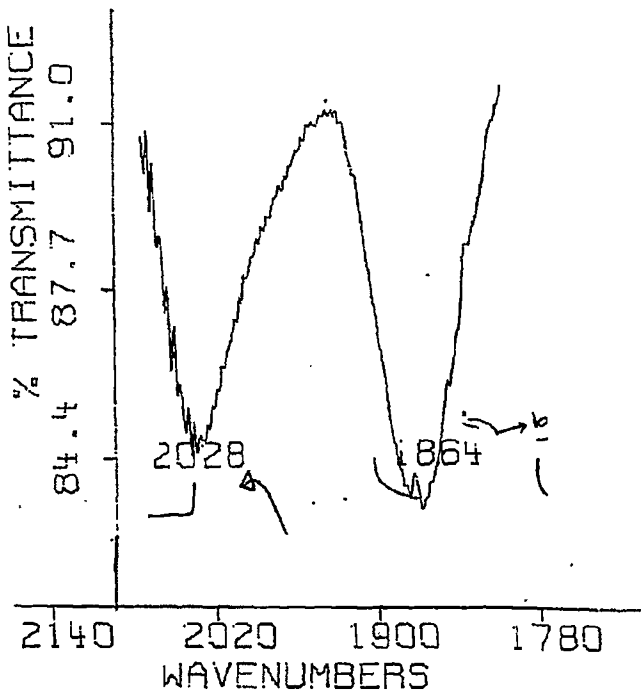


FIG. 3

INFRARED SPECTRA OF CO ON 3% Rh/ GAMMA ALUMINA



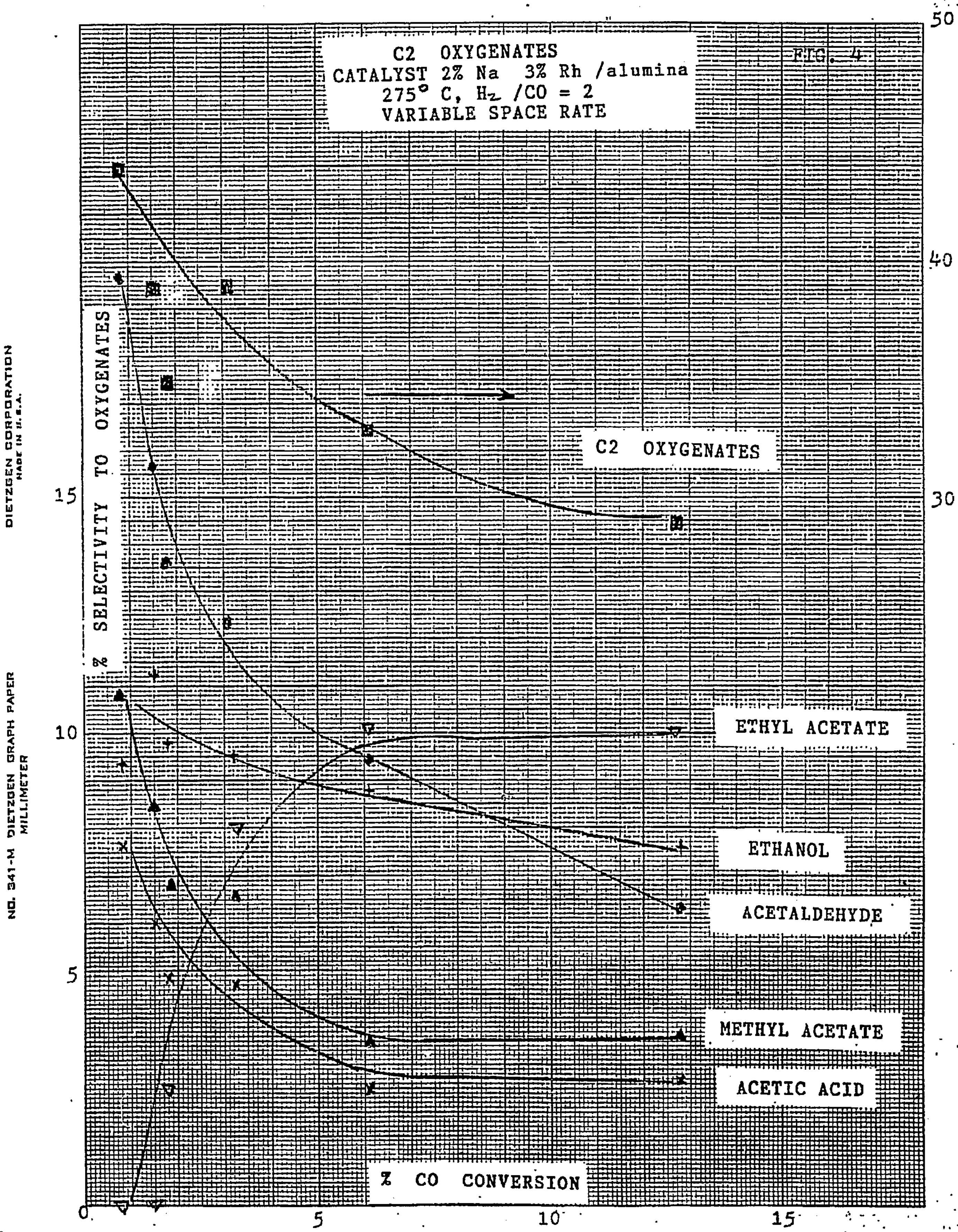
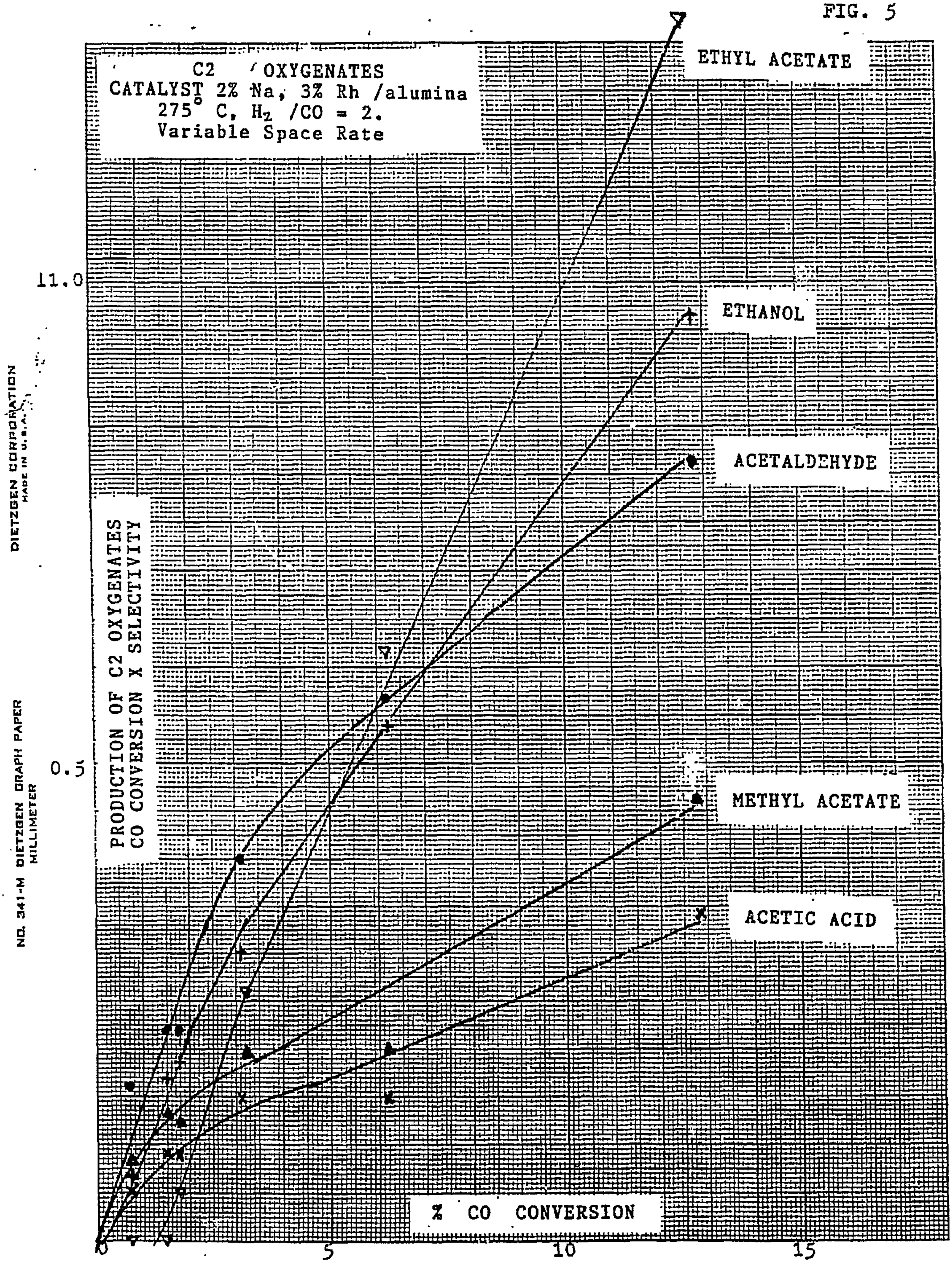

C2 OXYGENATES
CATALYST 2% Na 3% Rh /alumina
275° C, H2 /CO = 2
VARIABLE SPACE RATE
FIG. 4
% SELECTIVITY TO OXYGENATES
C2 OXYGENATES
ETHYL ACETATE
ETHANOL
ACETALDEHYDE
METHYL ACETATE
ACETIC ACID
% CO CONVERSION
0
5
10
15
30
40
50
DIETZGEN CORPORATION
MADE IN U.S.A.
NO. 341-M DIETZGEN GRAPH PAPER
MILLIMETER

FIG. 5



C2 OXYGENATES
CATALYST 2% Na, 3% Rh /alumina
275° C, H2 /CO = 2.
Variable Space Rate
ETHYL ACETATE
ETHANOL
ACETALDEHYDE
METHYL ACETATE
ACETIC ACID
PRODUCTION OF C2 OXYGENATES
CO CONVERSION X SELECTIVITY
% CO CONVERSION
11.0
0.5
0
5
10
15
DIETZGEN CORPORATION
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6

kinetic data

kinetic d

cat no (page no)	catalyst	temp C	pressure psig	CO:H2	GHSV hr-1	time hrs	%COconv incl CO2
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	250	450	0.5	3000	1	4.4
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	250	450	0.5	3000	12	2.8
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	250	450	0.5	1500	15	5.0
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	260	450	0.5	1500	18	6.9
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	250	750	0.5	1500	25	5.2
	Rh3%, 4.1%Ce/gamma Al203; H2-200,350,500C	250	450	0.5	1500	27	3.6
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	250	450	0.5	3000	1	0.7
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	250	450	0.5	1500	3	0.5
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	250	450	0.5	1500	3.5	0.4
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	275	450	0.5	1500	5	0.
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	275	450	0.5	1500	16	0.7
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	275	750	0.5	1500	20	1.1
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	275	450	0.5	1500	22	0.
	Rh3%, 3.6%Sn/Gamma Al203;from chlorides;H2-500C	275	450	0.5	1500	3	0.
	Rh1%/Gamma Al203 from Rh (II) acetate	150	450	0.5	1500	2	0.1
	Rh1%/Gamma Al203 from Rh (II) acetate	175	450	0.5	1500	4	0.
	Rh1%/Gamma Al203 from Rh (II) acetate	200	450	0.5	1500	7	0.
	Rh1%/Gamma Al203 from Rh (II) acetate	225	450	0.5	1800	10	1.
	Rh1%/Gamma Al203 from Rh (II) acetate	250	450	0.5	1500	13	3.
	Rh1%/Gamma Al203 from Rh (II) acetate	250	450	0.5	1500	27	2.
	Rh1%/Gamma Al203 from Rh (II) acetate	275	450	0.5	1500	29	8.
	Rh1%/Gamma Al203 from Rh (II) acetate	275	750	0.5	1500	31	10.
	Rh1%/Gamma Al203 from Rh (II) acetate	250	750	0.5	1500	34	3.
	Rh1%/Gamma Al203 from Rh (II) acetate	174	450	0.5	1500	46	
	Rh1%/Gamma Al203 from Rh (II) acetate	250	450	0.5	1500	2	6.
	Rh1%/Gamma Al203 from Rh (II) acetate	250	450	0.5	1500	18	3.
	Rh1%/Al203,from Rh(II)acetate;H2-200,350,500C	250	450	0.5	1500	14	3
	Rh1%/Al203,from Rh(II)acetate;H2-200,350,500C	275	450	0.5	1500	16	10
	Rh1%/Al203,from Rh(II)acetate;H2-200,350,500C	250	750	0.5	1500	20	4
	Rh1%/Al203,from Rh(II)acetate;H2-200,350,500C	250	450	0.5	1500	22	2.
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	450	0.5	1500	3	3.
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	450	0.5	1500	4.5	2.
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	450	0.5	1500	17	1
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	450	0.5	1500	23	2.
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	275	450	0.5	1500	43	4
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	275	450	0.5	1500	46	4
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	275	750	0.5	1500	49	7
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	275	750	0.5	1500	50	7
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	750	0.5	1500	54	2
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	750	0.5	1500	69	1
	Na1%/Reduced 3%Rh-Al203;dried 110C;H2-500C	250	450	0.5	1500	72	
	Rh3%/gamma Al203; new preparation; H2-500C	250	450	0.5	3000	1	[illegible]
	Rh3%/gamma Al203; new preparation; H2-500C	250	450	0.5	3000	8.5	[illegible]
	Rh3%/gamma Al203; new preparation; H2-500C	250	450	0.5	1500	68	[illegible]
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	0.5	3600	13	[illegible]
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	0.5	3600	24	[illegible]
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	0.5	1800	25.5	[illegible]
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	0.5	1800	26	[illegible]
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	750	0.5	3600	29	
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	260	750	0.5	3600	31	
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	0.5	1800	33	
	Rh3%/Gamma Al203 from RhCl3.3H2O; No calcination	250	450	1	1800	35	

kinetic data

%COconv incl CO2	time @ condition	CH4	C2H4	C2H6	C3H6	C3H8	MeOH	MeOMe	MeCHO	EtOH	C4H10	MeOAc
4.4	1	51.8	0.0	3.3	0.0	1.3	6.3	13.8	0.0	7.0	0.0	0.
2.8	12	51.0	0.0	2.3	0.0	0.0	9.9	9.4	0.0	11.9	0.0	1.
5.0	3	57.5	0.0	1.9	0.0	0.7	8.8	4.8	0.5	10.8	0.0	1.
6.9	2.5	63.7	0.0	3.4	0.0	1.3	6.2	2.9	0.3	9.1	0.6	1.
5.2	6	50.7	0.0	3.2	0.0	6.9	9.7	5.0	0.0	11.8	0.0	4.
3.6	2	55.4	0.0	4.0	0.0	1.3	8.9	4.4	0.0	10.0	0.0	3.
0.7	1	87.8	0.0	3.3	0.0	0.0	8.9	0.0	0.0	0.0	0.0	0.
0.5	2	96.0	0.0	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
0.4	2.5	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
0.9	1.5	89.8	0.0	10.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
0.7	13	98.2	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
1.1	3	88.9	0.0	11.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
0.6	2	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
0.8	3	88.6	0.0	11.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
0.1	2	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	EF
0.1	1.5	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	EF
0.3	2.5	2.6	0.0	6.3	0.0	0.0	14.7	25.1	0.0	11.3	0.0	0
1.2	3	3.1	0.0	15.2	1.6	7.9	3.1	9.4	0.0	4.7	3.2	0
3.2	3	68.5	0.0	10.5	0.0	4.1	0.7	5.7	0.0	5.3	2.3	0
2.5	14	72.2	0.0	7.5	0.0	3.9	0.8	3.2	2.3	6.0	1.8	0
8.5	2	76.5	0.0	7.9	0.0	2.4	0.5	3.5	1.7	4.9	1.2	0
10.6	2	76.4	0.0	7.5	0.0	1.9	0.4	3.0	2.6	3.8	0.9	0
3.2	3	73.2	0.0	6.9	0.0	4.3	0.9	2.9	4.2	3.4	1.1	2
.0	12	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
6.0	2	73.4	0.0	3.9	0.0	4.5	1.0	3.2	0.5	6.6	2.0	[illegible]
3.5	16	70.2	0.0	3.5	0.0	4.9	0.9	1.5	8.7	5.8	1.2	1
3.3	14	65.9	0.0	4.1	1.3	4.5	0.8	1.4	1.4	5.4	3.5	4
10.1	2	76.4	0.0	3.5	0.5	3.2	0.7	0.1	1.7	5.8	1.5	1
4.0	3	63.0	0.0	3.1	0.7	4.8	1.1	0.0	3.9	8.8	1.9	3
2.9	2	62.7	0.0	4.5	0.9	4.5	0.8	0.0	4.7	8.9	2.4	2
3.1	3	38.6	0.0	3.5	0.0	2.4	25.1	6.5	0.0	16.5	1.0	1
2.7	4.5	36.6	0.0	2.4	0.0	1.0	27.9	6.2	0.0	16.9	0.0	1
1.9	17	38.0	0.0	1.6	0.0	0.0	31.1	3.8	1.3	18.4	-0.0	1
2.0	23	39.3	0.0	3.6	0.0	1.6	25.2	2.2	2.2	17.1	0.0	[illegible]
4.5	20	59.7	0.0	4.7	0.0	1.8	8.1	0.0	3.4	11.1	0.0	[illegible]
4.5	23	59.2	0.0	5.4	0.0	2.2	8.2	0.0	3.5	10.9	0.0	[illegible]
7.9	3	52.6	0.0	6.3	0.0	2.6	7.2	0.0	2.4	14.2	0.0	[illegible]
7.3	3	55.1	0.0	5.8	0.0	2.6	8.2	0.0	2.7	10.7	0.0	[illegible]
2.0	4	38.7	0.0	4.3	0.0	1.5	18.1	0.0	3.3	13.6	0.0	1
1.8	15	38.5	0.0	4.2	0.0	1.8	23.2	1.2	3.5	12.7	0.0	[illegible]
0.9	3	40.2	0.0	3.8	0.0	1.7	17.8	1.2	5.0	14.0	0.0	[illegible]
6.6	1	65.5	0.0	4.7	0.0	3.7	0.9	3.1	0.4	8.1	2.0	[illegible]
5.7	8.5	59.7	0.0	4.2	0.0	5.1	1.9	1.1	1.9	11.3	2.0	[illegible]
9.1	48	62.6	0.0	3.8	0.6	3.7	1.5	0.3	2.2	9.7	1.4	[illegible]
6.1	2	57.6	0.0	3.5	1.5	4.1	0.8	0.1	4.1	10.6	1.7	[illegible]
4.8	12	59.0	0.0	2.9	1.5	3.5	0.9	0.4	4.2	10.3	1.1	[illegible]
9.2	1.5	61.2	0.0	3.2	1.0	3.5	0.8	0.0	4.2	9.9	0.9	[illegible]
8.9	2	61.6	0.0	3.2	1.2	3.6	0.7	0.1	3.5	9.9	1.0	[illegible]
5.2	3	58.2	0.0	2.9	0.8	3.4	1.2	0.0	5.1	10.4	1.3	[illegible]
7.9	2	62.7	0.0	3.1	1.2	4.0	1.0	0.2	3.6	8.7	1.3	[illegible]
7.5	2	60.7	0.0	2.7	0.9	3.8	1.1	0.1	3.5	10.2	1.5	[illegible]
3.9	2	49.8	0.0	3.6	2.1	4.3	1.0	0.0	4.9	13.0	1.9	[illegible]

kinetic data

kinetic data

EtOH	C4H10	MeOAc	AcOH	n-PrOH	EtCHO	C5H12	MeOEt	EtOAc	n-BuOH	i-BuOH	TOTALOXY C%,CO2fre
7.0	0.0	0.8	0.0	1.9	0.0	0.0	13.7	0.0	0.0	0.0	43.6
11.9	0.0	1.4	1.0	0.0	0.0	0.0	13.0	0.0	0.0	0.0	46.6
10.8	0.0	1.5	1.1	3.4	0.0	0.0	9.0	0.0	0.0	0.0	39.9
8.1	0.6	1.9	1.3	1.9	0.0	0.0	6.0	1.5	0.0	0.0	31.0
11.8	0.0	4.0	2.8	1.9	0.0	0.0	7.0	3.0	0.0	0.0	45.2
10.0	0.0	3.3	2.3	1.0	0.0	0.0	7.5	2.0	0.0	0.0	39.3
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.9
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.0
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR
11.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	51.1
4.7	3.2	0.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0	22.0
5.3	2.3	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	14.7
6.0	1.8	0.0	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.0	14.7
4.0	1.2	0.7	0.0	0.0	0.0	0.0	1.6	0.0	0.0	0.0	12.0
3.8	0.9	0.9	0.0	0.4	0.0	0.0	1.3	0.9	0.0	0.0	13.2
3.4	1.1	2.1	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	14.6
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.6	2.0	0.6	0.0	0.6	0.0	0.0	2.8	0.9	0.0	0.0	16.2
5.8	1.2	1.5	0.0	0.0	0.0	0.0	0.8	0.9	0.0	0.0	20.2
8.4	3.5	4.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0	20.7
5.8	1.5	1.2	0.0	1.9	0.0	0.4	2.0	0.9	0.0	0.0	14.4
8.8	1.9	3.6	0.0	1.7	0.0	0.0	2.9	3.7	1.0	0.0	26.6
8.9	2.4	2.3	0.0	1.4	0.0	0.0	3.4	3.5	0.0	0.0	25.0
16.5	1.0	1.4	1.0	0.0	0.0	0.0	4.0	0.0	0.0	0.0	54.6
16.9	0.0	1.5	1.1	0.0	0.0	0.0	6.4	0.0	0.0	0.0	60.0
18.4	0.0	1.0	0.7	0.0	0.0	0.0	4.2	0.0	0.0	0.0	60.4
17.1	0.0	4.2	3.1	0.0	0.0	0.0	1.5	0.0	0.0	0.0	55.4
11.1	0.0	4.3	3.1	0.0	0.0	0.0	0.0	3.8	0.0	0.0	33.8
10.9	0.0	4.2	2.9	0.0	0.0	0.0	0.0	3.5	0.0	0.0	33.2
14.2	0.0	5.2	3.7	1.8	0.0	0.0	0.0	3.9	0.0	0.0	38.5
10.7	0.0	5.7	4.0	1.0	0.0	0.0	0.0	4.3	0.0	0.0	36.5
13.6	0.0	10.2	7.1	0.0	0.0	0.0	0.0	3.9	0.0	0.0	55.5
12.7	0.0	9.9	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	57.5
14.6	0.0	9.5	6.7	0.0	0.0	0.0	0.0	0.6	0.0	0.0	54.3
8.1	2.0	0.0	0.0	3.3	0.0	1.5	6.9	0.0	0.0	0.0	22.6
11.3	2.0	3.4	0.0	2.7	0.4	0.0	3.0	3.3	0.0	0.0	28.9
9.7	1.4	2.4	0.0	2.2	0.0	0.4	2.1	6.4	0.7	0.0	27.5
10.6	1.7	4.5	0.0	2.3	0.3	0.3	2.7	5.9	0.0	0.0	31.3
10.3	1.1	4.5	0.0	1.9	0.0	0.0	1.5	8.3	0.0	0.0	32.1
9.9	0.9	3.4	0.0	2.2	0.0	0.2	1.4	7.4	0.8	0.0	30.0
9.9	1.0	3.3	0.0	1.9	0.0	0.0	1.4	7.8	0.8	0.0	29.4
10.4	1.3	6.1	0.0	1.7	0.0	0.0	1.7	6.3	0.9	0.0	33.4
8.7	1.3	4.5	0.0	1.1	0.0	0.0	1.8	5.8	0.9	0.0	27.7
10.2	1.5	3.7	0.0	2.0	0.0	0.0	2.1	6.9	0.8	0.0	30.4
13.0	1.9	4.7	0.0	1.7	0.0	0.0	2.6	9.4	0.9	0.0	38.2

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HYDRO C% C1	c2	C3	c4	oxyg C% C1	C2	C3	C4	turnover no. sec-1	%C2+OXG of total	RATE CO gmol/hr	C% to CO2 CO2 incl	COMM
51.8	3.3	1.3	0.0	25.0	16.6	1.9	0.0	1.73E-03	42.7	1.1E-03	11.1	From
51.0	2.3	0.0	0.0	24.1	22.4	0.0	0.0	1.10E-03	48.4	6.9E-04	5.2	alm
57.5	1.9	0.7	0.0	17.1	19.3	3.4	0.0	9.74E-04	57.1	6.1E-04	6.3	Cont
63.7	3.4	1.3	0.6	11.7	17.4	1.9	0.0	1.35E-03	62.4	8.5E-04	6.4	
50.7	3.2	0.9	0.0	18.3	24.9	1.9	0.0	1.00E-03	59.4	6.3E-04	6.2	Act
55.4	4.0	1.3	0.0	16.8	21.4	1.6	0.0	7.00E-04	57.2	4.4E-04	5.3	Orig
87.8	3.3	0.0	0.0	8.9	0.0	0.0	0.0	2.87E-04	.0	1.8E-04	8.7	Cata
96.0	4.0	0.0	0.0	0.0	0.0	0.0	0.0	9.50E-05	~~100.0~~	6.0E-05	23.4	loo
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.29E-05	ERR	5.2E-05	22.6	
89.8	10.2	0.0	0.0	0.0	0.0	0.0	0.0	1.81E-04	ERR	1.1E-04	33.0	cont
98.2	1.8	0.0	0.0	0.0	0.0	0.0	0.0	1.31E-04	~~100.0~~	8.3E-05	36.9	
88.9	11.1	0.0	0.0	0.0	0.0	0.0	0.0	2.17E-04	~~100.0~~	1.4E-04	36.6	aft
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.17E-04	ERR	7.4E-05	39.5	aft
88.6	11.4	0.0	0.0	0.0	0.0	0.0	0.0	1.63E-04	~~100.0~~	1.0E-04	37.1	Repr
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	4.92E-05	ERR	1.0E-05	100.0	No ca
ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	3.56E-05	ERR	7.5E-06	100.0	the
42.6	6.3	0.0	0.0	39.8	11.3	0.0	0.0	1.75E-04	22.0	3.7E-05	21.7	most
50.1	15.2	9.5	3.2	14.0	7.9	0.0	0.0	8.13E-04	36.1	1.4E-04	5.8	
68.5	10.5	4.1	2.3	7.3	7.3	0.0	0.0	1.87E-03	50.0	3.9E-04	5.4	
72.2	7.5	3.9	1.8	4.8	9.8	0.0	0.0	1.48E-03	66.9	3.1E-04	3.1	
76.5	7.9	2.4	1.2	4.7	7.2	0.0	0.0	4.94E-03	60.3	1.0E-03	1.4	
76.4	7.5	1.9	0.9	4.1	8.7	0.4	0.0	6.21E-03	69.0	1.3E-03	1.7	actua
73.2	6.9	4.3	1.1	4.8	9.7	0.0	0.0	1.84E-03	67.0	3.9E-04	1.8	after
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.55E-05	ERR	3.3E-06	0.0	After
73.4	3.9	4.5	2.0	5.3	10.3	0.6	0.0	3.48E-03	67.1	7.3E-04	4.4	
70.2	3.5	4.9	1.2	3.2	16.9	0.0	0.0	2.07E-03	84.2	4.3E-04	1.7	End
65.9	4.1	5.8	3.5	5.1	15.6	0.0	0.0	1.92E-03	75.5	4.0E-04	2.7	No c
76.4	3.5	3.7	1.5	1.9	10.6	1.9	0.0	5.88E-03	86.7	1.2E-03	1.7	Comb
63.0	3.1	5.4	1.9	3.3	20.6	1.7	1.0	2.32E-03	87.8	4.9E-04	1.6	Comb
62.7	4.5	5.4	2.4	2.7	20.8	1.4	0.0	1.70E-03	89.3	3.6E-04	2.0	End
38.6	3.5	2.4	1.0	33.4	21.1	0.0	0.0	5.96E-04	38.7	3.8E-04	27.5	propa
36.6	2.4	1.0	0.0	36.7	23.2	0.0	0.0	5.35E-04	38.8	3.4E-04	25.0	Comb
38.0	1.6	0.0	0.0	36.6	23.8	0.0	0.0	3.77E-04	39.4	2.4E-04	15.5	CO2
39.3	3.6	1.6	0.0	29.3	26.0	0.0	0.0	3.81E-04	47.1	2.4E-04	12.7	incr
59.7	4.7	1.8	0.0	9.5	24.2	0.0	0.0	8.68E-04	71.8	5.5E-04	9.9	Ether
59.2	5.4	2.2	0.0	9.6	23.6	0.0	0.0	8.76E-04	71.2	5.5E-04	9.6	incre
52.6	6.3	2.6	0.0	8.9	27.7	1.8	0.0	1.54E-03	76.8	9.7E-04	13.6	
55.1	5.8	2.6	0.0	10.0	25.4	1.0	0.0	1.42E-03	72.5	8.9E-04	14.2	proba
38.7	4.3	1.5	0.0	21.4	34.0	0.0	0.0	3.97E-04	61.4	2.5E-04	10.5	ran o
36.5	4.2	1.8	0.0	27.7	29.7	0.0	0.0	3.45E-04	51.9	2.2E-04	12.3	Ethyl
40.2	3.8	1.7	0.0	22.2	32.0	0.0	0.0	1.73E-04	59.2	1.1E-04	8.1	Origin
65.5	4.7	3.7	2.6	6.3	13.1	3.3	0.0	2.55E-03	72.3	1.6E-03	3.9	catal
59.7	4.2	5.1	2.0	5.1	20.7	3.0	0.0	2.20E-03	82.4	1.4E-03	0.9	Combin
62.6	3.8	4.3	1.4	3.3	21.3	2.2	0.7	1.77E-03	87.9	1.1E-03	1.4	no AcC
57.6	3.5	5.6	1.7	3.3	25.3	2.6	0.0	2.83E-03	89.4	1.5E-03	0.6	No cal
59.0	2.9	4.9	1.1	3.3	26.8	1.9	0.0	2.24E-03	89.7	1.2E-03	0.5	React
61.2	3.2	4.5	0.9	2.3	24.6	2.2	0.8	2.16E-03	92.2	1.1E-03	0.9	Combin
61.6	3.2	4.8	1.0	2.4	24.3	1.9	0.8	2.08E-03	91.9	1.1E-03	0.8	Combin
58.2	2.9	4.1	1.3	3.8	27.0	1.7	0.9	2.45E-03	88.6	1.3E-03	0.7	Combin
62.7	3.1	5.3	1.3	3.3	22.3	1.1	0.9	3.69E-03	88.1	1.9E-03	0.9	after
60.7	2.7	4.7	1.5	3.1	24.5	2.0	0.8	1.76E-03	89.8	9.2E-04	0.8	now,
49.8	3.6	6.4	1.9	3.4	32.1	1.7	0.9	1.36E-03	91.2	7.1E-04	1.2	End of

kinetic data

TABLE I

	turnover no. sec-1	%C2+OXG of total	RATE CO gmol/hr	C% to CO2 CO2 incl	COMMENTS
.0	1.73E-03	42.7	1.1E-03	11.1	From previous expt. on the same catalyst, from Porapak T analysis,
.0	1.10E-03	48.4	6.9E-04	5.2	almost no propane or butane are formed on this catalyst.
.0	9.74E-04	57.1	6.1E-04	6.3	Combined (AcOH+MeOAc) peak : ratio of AcOH to MeOAc is taken as 1:1
.0	1.35E-03	62.4	8.5E-04	6.4	
.0	1.00E-03	59.4	6.3E-04	6.2	Actual space velocity may be about 15% lower, because of small leak
.0	7.00E-04	57.2	4.4E-04	5.3	Original condition; End of reaction.
.0	2.87E-04	.0	1.8E-04	8.7	Catalyst not calcined. Directly reduced in H2 at 200,350 and 500C
.0	9.50E-05	~~100.0~~	6.0E-05	23.4	looks like rapid deactivation
.0	8.29E-05	ERR	5.2E-05	22.6	
.0	1.81E-04	ERR	1.1E-04	33.0	continued overnight
.0	1.31E-04	~~100.0~~	8.3E-05	36.9	
.0	2.17E-04	~~100.0~~	1.4E-04	36.6	after this, went back to the original condition
.0	1.17E-04	ERR	7.4E-05	39.5	after this, cut off CO, cooled to room temp. After weekend, started rexn
.0	1.63E-04	~~100.0~~	1.0E-04	37.1	Reproducible; End of reaction
RR	4.92E-05	ERR	1.0E-05	100.0	No calcination; NO REDUCTION; Heated to 150C in H2, immediately started rexn
.R	3.56E-05	ERR	7.5E-06	100.0	the reaction at 450psia.
.0	1.75E-04	22.0	3.7E-05	21.7	most of the small peak areas are not accurate
.0	8.13E-04	36.1	1.4E-04	5.8	
.0	1.87E-03	50.0	3.9E-04	5.4	
.0	1.48E-03	66.9	3.1E-04	3.1	
.0	4.94E-03	60.3	1.0E-03	1.4	
.0	6.21E-03	69.0	1.3E-03	1.7	actual space velocity may be lower by about 20% because of leak
.0	1.84E-03	67.0	3.9E-04	1.8	after this, reduced the temp. to 174C, pressure to 450psia
.0	1.55E-05	ERR	3.3E-06	0.0	After this CO cut off, H2 reduced : 275-.5hr,350-1hr,500C-1hr
.0	3.48E-03	67.1	7.3E-04	4.4	
.0	2.07E-03	84.2	4.3E-04	1.7	End of the reaction
.0	1.92E-03	75.5	4.0E-04	2.7	No calcination; H2 reduced directly;2/3 of combined peak is propane
.0	5.88E-03	86.7	1.2E-03	1.7	Combined (C4H10+MeOEt)peak : 30% area is butane, rest MeOEt
.0	2.32E-03	87.8	4.9E-04	1.6	Combined (AcOH+MeOAc)peak : all AcOH, no MeOAc
.0	1.70E-03	89.3	3.6E-04	2.0	End of the reaction.
.0	5.96E-04	38.7	3.8E-04	27.5	propane and butane areas are approximated roughly
.0	5.35E-04	38.8	3.4E-04	25.0	Combined (AcOH+MeOAc) peak : area ratio approximated as 1:1
.0	3.77E-04	39.4	2.4E-04	15.5	CO2 formation has drastically reduced
.0	3.81E-04	47.1	2.4E-04	12.7	increased the temp to 275C and ran overnight
.0	8.68E-04	71.8	5.5E-04	9.9	Ethers disappeared, CH3CHO appeared
.0	8.76E-04	71.2	5.5E-04	9.6	increased the pressure to 750psia
.0	1.54E-03	76.8	9.7E-04	13.6	
.0	1.42E-03	72.5	8.9E-04	14.2	probably this ethanol area is right
.0	3.97E-04	61.4	2.5E-04	10.5	ran overnight at this condition
0.9	3.45E-04	51.9	2.2E-04	12.3	Ethyl acetate disappeared
.0	1.73E-04	59.2	1.1E-04	8.1	Original condition; End of reaction.
.0	2.55E-03	72.3	1.6E-03	3.9	catalyst calcined at 500C before;
.0	2.20E-03	82.4	1.4E-03	0.9	Combined (C4H10+MeOEt)peak : 30% area is butane
.7	1.77E-03	87.9	1.1E-03	1.4	no AcOH, all MeOAc; End of reaction.
.0	2.83E-03	89.4	1.5E-03	0.6	No calcination step; catalyst reduced in H2 at 400C-1hr
.0	2.24E-03	89.7	1.2E-03	0.5	Reaction first started at 225C, ran for 12hrs, but data is not good
.6	2.16E-03	92.2	1.1E-03	0.9	Combined (propane+methanol) peak : 2/3 area is propane, rest MeOH
0.8	2.08E-03	91.9	1.1E-03	0.8	Combined (C4H10+MeOEt) peak : 30% area is butane, rest MeOEt
.9	2.45E-03	88.6	1.3E-03	0.7	Combined (AcOH+MeOAc) peak : all area is MeOAc, no AcOH
.9	3.69E-03	88.1	1.9E-03	0.9	after this, went back to the original condition
.8	1.76E-03	89.8	9.2E-04	0.8	now, tried H2:CO=1:1 just to see
.9	1.36E-03	91.2	7.1E-04	1.2	End of reaction

KINETIC DATA

cat no (page no)	catalyst	temp C	pressure psig	CO:H2	GHSV hr-1	time hrs	%COconv incl CO2
	Rh5%/High purity Gamma Al2O3, J.-M.	225	450	0.5	3333	2	3.[illegible]
	Rh5%/High purity Gamma Al2O3, J.-M.	250	450	0.5	3333	4.3	7.6[illegible]
	Rh5%/High purity Gamma Al2O3, J.-M.	250	450	0.5	1667	20	10.7[illegible]
	Rh5%/High purity Gamma Al2O3, J.-M.	250	750	1	2222	22	5.6[illegible]
	Na1%/reduced 5%Rh-Al2O3, J.-M.	250	450	0.5	1500	2.7	5.[illegible]
	Na1%/reduced 5%Rh-Al2O3, J.-M.	275	450	0.5	1500	8	7.[illegible]
	Na1%/reduced 5%Rh-Al2O3, J.-M.	275	450	0.5	1500	23	7.2[illegible]
	Na1%/reduced 5%Rh-Al2O3, J.-M.	275	750	0.5	1500	26	9.3[illegible]
	Na1%/reduced 5%Rh-Al2O3, J.-M.	250	750	0.5	1500	29	2.7[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	250	450	0.5	3000	2	7.[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	450	0.5	3000	3	20.[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	450	1	2000	4	13.[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	450	1	2000	20	8.8[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	450	0.5	3000	21	12.5[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	710	0.5	3000	23	15.7[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	290	710	0.5	3000	25	28.6[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	450	0.5	3000	26	12.[illegible]
	Rh3%/Gamma Al2O3(catapal),from Engel.NO3 soln.	275	200	0.5	3000	27	8.6[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	3000	2	3.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	3000	15	2.5[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	275	450	0.5	3000	17	8.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	284.5	450	0.5	3000	18	12.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	3000	22	2.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	1500	24	4.4[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	1500	26	4.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	450	0.5	3000	1.5	3.1[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	250	710	0.5	3000	4.5	3.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	275	710	0.5	3000	6	11.[illegible]
	Rh3%,.67%Na/Gamma Al2O3,coimprg.	275	200	0.5	3000	7	6.1[illegible]
	Rh3%,2%Na/Al2O3;He-120,H2-200,350,500C	250	450	0.5	3600	1	0.[illegible]
	Rh3%,2%Na/Al2O3;He-120,H2-200,350,500C	276	450	0.5	3600	4	1.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	250	450	0.5	1500	3	1.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	250	450	0.5	1500	19	1.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	275	450	0.5	1500	21	3.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	275	750	0.5	1500	23	3.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	250	750	0.5	1500	25	1.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	250	750	1	2000	27	0.[illegible]
	Rh3%,2%Na/Al2O3;Air-500,H2-200,350,500C	275	750	1	2000	29	1.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	250	450	0.5	3273	1	2.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	250	450	0.5	3273	1.6	2.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	250	450	0.5	3273	21	1.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	275	450	0.5	3273	23	5.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	285.5	450	0.5	3273	25	6.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	275	750	0.5	3273	26	6.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	250	750	0.5	3273	28	1.[illegible]
	Rh3%,1.14%K/Al2O3;Air-500,H2-200,350,500C	250	200	0.5	1636	29	1.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	409	48	12.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	818	50	6.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	1636	52	3.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	2455	71	1.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	3273	78	1.[illegible]
	3% Rh 2% Na/Al2O3calc in air	275	450	0.5	3927	96	0.[illegible]
	Rh3%/Al2O3, red.at 500C;	250	450	0.5	8571	45	2.[illegible]
	Rh3%/Al2O3, red at 500C	250	450	0.5	12857	48	1[illegible]
	Rh3%/Al2O3, red at 500C	250	450	0.5	17143	50	1.[illegible]

KINETIC DATA

CO:H2	GHSV hr-1	time hrs	%COconv incl CO2	time @ condition	SELECTIVITY IN PRODUCTS CARBON%							
					CH4	C2H4	C2H6	C3H6	C3H8	MeOH	MeOMe	MeCHO
0.5	3333	2	3.0	2	56.0	0.0	2.9	0.0	5.7	1.1	0.0	3.7
0.5	3333	4.3	7.6	1.5	61.1	0.0	3.1	0.0	4.8	0.9	0.0	1.9
0.5	1667	20	10.7	15	62.2	0.0	2.7	0.0	3.0	0.6	0.0	2.7
1	2222	22	5.6	2	47.8	0.0	2.1	0.0	3.3	0.6	0.0	5.5
0.5	1500	2.7	5.0	2.7	43.4	0.0	2.4	0.0	1.0	12.0	0.0	0.6
0.5	1500	8	7.9	4	63.2	0.0	2.2	0.0	0.9	2.7	0.0	1.4
0.5	1500	23	7.2	15	60.8	0.0	1.9	0.0	0.8	4.0	0.0	1.3
0.5	1500	26	9.3	2	54.3	0.0	1.6	0.0	0.7	6.8	0.0	1.7
0.5	1500	29	2.7	3	33.2	0.0	0.4	0.0	0.2	14.6	0.0	1.4
0.5	3000	2	7.4	2	60.9	0.0	5.3	0.0	5.9	1.2	2.2	0.0
0.5	3000	3	20.7	1	73.4	0.0	5.0	0.3	4.6	0.9	0.2	1.1
1	2000	4	13.2	1	63.0	0.0	5.2	1.0	5.2	1.0	.0	2.1
1	2000	20	8.8	16	61.0	0.0	4.9	2.2	5.2	1.0	0.0	3.1
0.5	3000	21	12.5	1	67.8	0.0	4.1	0.9	4.1	0.8	0.2	2.3
0.5	3000	23	15.7	1.5	69.2	0.0	4.6	1.0	4.8	0.9	0.2	2.0
0.5	3000	25	28.6	1.5	76.8	0.0	4.7	0.5	4.9	0.9	0.1	1.1
.5	3000	26	12.3	1	66.8	0.0	5.2	0.9	4.8	0.9	0.1	1.8
0.5	3000	27	8.6	1	64.9	0.0	4.4	1.1	5.6	1.1	0.0	1.5
0.5	3000	2	3.2	2	55.8	0.0	4.2	0.0	1.7	7.5	3.8	0.0
.5	3000	15	2.5	15	55.7	0.0	5.3	0.0	2.2	4.8	0.0	4.8
0.5	3000	17	8.2	1	68.5	0.0	5.1	0.5	2.1	2.8	0.0	2.8
.5	3000	18	12.4	1	71.0	0.0	6.2	0.5	2.6	2.1	0.0	2.2
.5	3000	22	2.3	1	56.3	0.0	5.0	3.3	2.1	3.8	0.0	4.8
.5	1500	24	4.4	1	58.4	0.0	6.1	1.6	2.5	3.5	0.0	5.7
.5	1500	26	4.4	1.5	58.3	0.0	7.1	1.5	3.0	3.0	0.0	5.0
.5	3000	1.5	3.1	1.5	57.6	0.0	5.5	2.9	2.3	5.1	0.0	0.6
0.5	3000	4.5	3.3	3	54.9	0.0	4.9	2.3	2.0	5.1	0.0	3.3
.5	3000	6	11.4	1.5	62.4	0.0	5.6	1.1	2.3	2.4	0.0	4.2
.5	3000	7	6.1	1	74.8	0.0	3.2	2.5	1.3	2.1	0.0	3.2
.5	3600	1	0.9	1	29.5	0.0	0.0	0.0	0.0	41.3	0.0	0.0
.5	3600	4	1.7	2.5	41.2	0.0	1.6	0.0	0.0	28.1	0.0	0.0
0.5	1500	3	1.8	1.4	31.9	0.0	2.7	0.0	0.0	39.5	0.0	0.0
.5	1500	19	1.0	17	29.3	0.0	0.0	0.0	0.0	42.2	0.0	0.0
.5	1500	21	3.3	1.5	42.9	0.0	3.4	0.0	0.0	18.3	0.0	2.7
.5	1500	23	3.4	2	42.5	0.0	1.7	0.0	0.0	22.8	0.0	2.7
.5	1500	25	1.0	2	26.9	0.0	0.0	0.0	0.0	39.0	0.0	1.9
1	2000	27	0.4	2	22.4	0.0	0.0	0.0	0.0	41.7	0.0	3.3
1	2000	29	1.0	1.6	32.8	0.0	4.0	0.0	0.0	25.7	0.0	8.7
.5	3273	1	2.7	1	56.2	0.0	5.0	0.0	2.0	9.7	5.5	0.0
.5	3273	1.6	2.5	1.6	56.0	0.0	5.5	0.0	2.2	8.9	4.5	0.0
.5	3273	21	1.6	21	52.2	0.0	7.3	0.0	2.9	8.1	0.0	5.8
.5	3273	23	5.5	2	66.4	0.0	5.4	0.0	2.2	5.7	0.0	3.8
.5	3273	25	8.4	1.3	72.4	0.0	5.6	0.6	2.3	2.3	0.3	2.6
.5	3273	26	6.3	1.3	65.3	0.0	6.5	0.0	2.7	3.1	0.0	3.9
.5	3273	28	1.9	1.3	49.6	0.0	3.5	0.0	1.6	6.2	0.0	8.7
.5	1636	29	1.7	1	66.4	0.0	2.5	0.0	0.9	3.1	0.0	5.5
.5	409	48	12.8	48	60.7	0.0	4.3	0.0	1.7	1.2	0.0	6.3
.5	818	50	6.1	2	55.8	0.0	4.0	0.0	1.6	1.9	0.0	9.4
.5	1636	52	3.2	2	47.8	0.0	4.3	0.0	1.7	3.3	0.0	12.4
.5	2455	71	1.8	19	49.8	0.0	4.4	0.0	2.0	3.6	0.0	13.6
.5	3273	78	1.5	7	51.4	0.0	0.0	0.0	0.0	4.7	0.0	15.8
.5	3927	96	0.8	18	45.3	0.0	0.0	0.0	0.0	5.1	0.0	19.8
.5	8571	45	2.2	45	56.0	0.0	3.3	1.8	5.4	1.2	1.4	3.6
.5	12857	48	1.5	2	54.2	0.0	2.3	1.4	5.4	1.1	1.7	4.9
.5	17143	50	1.0	2	50.9	0.0	2.4	1.9	5.7	1.3	3.7	6.3

KINETIC DATA

	MeCHO	EtOH	C4H10	MeOAc	AcOH	n-PrOH	EtCHO	C5H12	MeOEt	EtOAc	n-BuOH	i-BuOH	TOTALOXY C%,CO2f
0	3.7	19.6	2.4	4.8	0.0	0.0	0.0	0.0	3.7	0.0	0.0	0.0	32.
[illegible]	1.9	16.5	1.3	1.6	0.0	4.6	0.0	0.0	2.1	2.0	0.0	0.0	29.
0	2.7	11.6	0.9	2.7	0.0	4.1	0.0	0.0	1.4	8.2	0.0	0.0	31.
0	5.5	14.7	1.3	4.6	0.0	3.5	0.0	1.2	1.9	13.5	0.0	0.0	44.
[illegible]	0.6	32.4	0.0	2.1	1.5	0.0	1.8	0.0	0.0	2.8	0.0	0.0	53.2
[illegible]	1.4	14.8	0.0	3.6	2.6	0.0	0.5	0.0	0.0	7.9	0.0	0.0	33.6
[illegible]	1.3	16.9	0.0	4.1	2.9	0.0	0.6	0.0	0.0	6.5	0.0	0.0	36.4
[illegible]	1.7	14.7	0.0	6.5	4.6	0.0	0.3	0.0	0.0	8.7	0.0	0.0	43.4
[illegible]	1.4	20.2	0.0	11.4	8.1	0.0	0.0	0.0	0.0	10.5	0.0	0.0	66.2
2	0.0	7.7	4.0	0.0	0.0	4.3	0.0	2.3	6.2	0.0	0.0	0.0	21.
2	1.1	5.3	1.6	0.5	0.0	2.4	0.0	0.7	2.4	0.9	0.6	0.0	14.
[illegible]	2.1	6.4	1.6	1.8	0.0	2.5	0.2	1.2	2.4	3.7	2.6	0.0	22.
[illegible]	3.1	5.4	1.5	2.2	0.0	2.5	0.1	2.4	2.3	5.1	1.2	0.0	22.
2	2.3	5.1	1.4	2.6	0.0	2.5	0.0	1.9	2.1	3.6	0.6	0.0	19.
2	2.0	3.7	1.5	2.3	0.0	2.0	0.0	1.5	2.2	3.3	0.7	0.0	17.
1	1.1	2.3	1.1	1.2	0.0	0.9	0.2	1.2	1.7	2.2	0.3	0.0	10.9
1	1.8	6.9	1.5	1.7	0.0	2.3	0.0	1.3	2.2	2.9	0.6	0.0	19.5
[illegible]	1.5	10.2	1.0	2.4	0.0	2.8	0.0	1.0	1.5	2.1	0.4	0.0	22.
[illegible]	0.0	13.3	0.8	1.3	0.0	4.7	0.0	0.0	6.8	0.0	0.0	0.0	37.5
[illegible]	4.8	13.8	0.0	4.0	2.8	2.1	0.0	0.0	0.0	4.5	0.0	0.0	36.
[illegible]	2.8	8.5	0.6	1.9	1.4	0.9	0.0	0.0	0.8	3.5	0.8	0.0	23.
[illegible]	2.2	7.7	1.4	0.8	0.6	0.5	0.3	0.5	0.9	2.7	0.0	0.0	17.
[illegible]	4.8	14.0	0.0	3.1	2.2	0.0	0.0	0.0	0.0	5.4	0.0	0.0	33.
[illegible]	5.7	12.2	1.1	1.8	1.3	0.0	0.0	0.0	0.9	5.0	0.0	0.0	30.
0	5.0	12.5	0.9	1.7	1.2	0.0	0.0	0.0	0.8	5.0	0.0	0.0	29.
0	0.6	18.3	1.0	0.0	0.0	3.8	0.0	0.0	2.9	0.0	0.0	0.0	30.
[illegible]	3.3	18.0	1.2	0.0	0.0	2.3	0.0	0.0	1.8	0.9	3.4	0.0	34.7
0	4.2	8.8	1.1	1.6	1.1	1.2	0.5	0.8	0.4	4.0	2.5	0.0	26.7
0	3.2	7.5	0.8	0.6	0.5	0.0	0.0	0.0	1.0	2.5	0.0	0.0	17.
0	0.0	13.2	0.0	9.4	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	70.
0	0.0	20.0	0.0	5.3	3.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	57.2
0	0.0	25.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	65.
0	0.0	28.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	70.7
0	2.7	20.4	0.0	3.4	2.4	6.4	0.0	0.0	0.0	0.0	0.0	0.0	53.
0	2.7	18.3	0.0	4.7	3.3	4.0	0.0	0.0	0.0	0.0	0.0	0.0	55.8
0	1.9	18.6	0.0	8.0	5.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	73.1
0	3.3	19.7	0.0	7.5	5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77.6
0	8.7	13.6	0.0	8.9	6.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	63.3
.5	0.0	12.4	1.2	1.5	0.9	0.0	0.0	0.0	5.7	0.0	0.0	0.0	35.6
.5	0.0	13.3	1.3	1.6	0.9	0.0	0.0	0.0	5.8	0.0	0.0	0.0	35.1
0	5.8	13.8	0.0	4.4	3.1	0.0	0.0	0.0	0.0	2.2	0.0	0.0	37.6
0	3.8	7.6	0.7	2.9	2.0	0.0	1.1	0.0	0.3	1.9	0.0	0.0	25.3
.3	2.6	5.9	0.9	1.8	1.3	0.6	0.6	0.0	0.0	2.9	0.0	0.0	18.3
0	3.9	7.1	0.9	3.2	2.2	0.0	0.9	0.0	0.0	4.2	0.0	0.0	24.
.0	8.7	10.7	0.0	7.5	5.3	0.0	2.0	0.0	0.0	4.1	0.0	0.0	45.3
.0	5.5	11.7	0.0	3.9	2.8	0.0	0.0	0.0	0.0	3.2	0.0	0.0	30.2
.0	6.3	7.6	0.0	3.7	2.6	0.0	1.8	0.0	0.0	10.0	0.0	0.0	33.3
.0	9.4	8.8	0.0	3.5	2.5	0.0	2.4	0.0	0.0	10.1	0.0	0.0	38.6
.0	12.4	9.5	0.0	6.7	4.8	0.0	1.4	0.0	6.0	8.0	0.0	0.0	46.2
.0	13.6	9.8	0.0	6.9	4.9	0.0	2.5	0.0	0.0	2.5	0.0	0.0	43.
.0	15.8	11.2	0.0	8.5	6.0	0.0	2.4	0.0	0.0	0.0	0.0	0.0	48.6
.0	19.8	9.3	0.0	10.9	7.7	0.0	2.0	0.0	0.0	0.0	0.0	0.0	54.7
.4	3.6	8.6	2.3	4.1	0.0	2.8	1.7	0.0	3.3	4.5	0.0	0.0	31.
.7	4.9	8.5	2.7	5.1	0.0	3.1	0.0	0.0	3.8	5.8	0.0	0.0	34.
.7	6.3	7.4	2.9	7.3	0.0	3.0	0.0	0.0	4.1	3.0	0.0	0.0	36.1

KINETIC DATA

MeOEt	EtOAc	n-BuOH	i-BuOH	TOTALOXY C%,CO2fre	%C2+OXG of total	RATE CO gmol/hr	C% to CO2 CO2 incl	
3.7	0.0	0.0	0.0	32.9	88.1	7.4E-04	5.0	Combined (C3H8+MeOH) area : 2/3 is propane,
2.1	2.0	0.0	0.0	29.6	92.7	1.9E-03	1.8	Combined (C4H10+MeOEt) area : 30% Butane, r
1.4	8.2	0.0	0.0	31.2	93.9	1.3E-03	1.3	Combined (AcOH+MeOAc) area : all MeOAc, No
1.9	13.5	0.0	0.0	44.4	93.7	1.4E-03	1.9	End of reaction
0.0	2.8	0.0	0.0	53.2	76.2	6.1E-04	21.4	Na deposited as NaOH on as-recieved catalys
0.0	7.9	0.0	0.0	33.6	88.3	9.7E-04	7.7	Catalyst reduced in H2 flow at 300C for 2
0.0	6.5	0.0	0.0	36.4	85.2	8.8E-04	7.4	Combined (C3H8+MeOH) peak : 35% of C2H6 pe
0.0	8.7	0.0	0.0	43.4	79.3	1.1E-03	10.0	Combined (AcOH+MeOAc) peak : approximate ra
0.0	10.5	0.0	0.0	66.2	72.2	3.4E-04	7.3	reaction stopped
6.2	0.0	0.0	0.0	21.6	75.0	1.9E-03	3.5	Butane area is 30% of the combined (C4H10+M
2.4	0.9	0.6	0.0	14.4	85.3	5.1E-03	2.2	Combined (MeOH+C3H8) peak : 2/3 area is pr
2.4	3.7	2.6	0.0	22.9	89.3	3.3E-03	2.8	Combined (AcOH+MeOAc) peak : No AcOH, all
2.3	5.1	1.2	0.0	22.8	89.1	2.2E-03	2.0	After overnight at previous condition
2.1	3.6	0.6	0.0	19.7	87.0	3.1E-03	1.1	Changed back to CO:H2=1:2
2.2	3.3	0.7	0.0	17.3	84.9	3.9E-03	1.5	Higher pressure
1.7	2.2	0.3	0.0	10.9	81.6	7.1E-03	2.2	MeOH peak area may be lower than calculat
2.2	2.9	0.6	0.0	19.5	87.9	3.1E-03	1.1	redn 50cc/min H2 350C(.5hr
1.5	2.1	0.4	0.0	22.0	89.2	2.1E-03	0.6	End of the reaction
6.8	0.0	0.0	0.0	37.5	62.6	7.8E-04	10.6	Calcined 500C,H2-200C.5hr,350 .5hr,500C 1hr
0.0	4.5	0.0	0.0	36.7	83.4	6.2E-04	1.9	Propane area is 35% of C2H6 peak area;
0.8	3.5	0.8	0.0	23.3	83.9	2.0E-03	2.6	Combined (AcOH+MeOAc) peak : AcOH-MeOAc ra
0.9	2.7	0.0	0.0	17.8	84.8	3.1E-03	2.4	Butane area - rough approximation
0.0	5.4	0.0	0.0	33.4	85.5	5.6E-04	2.7	Original starting condition.
0.9	5.0	0.0	0.0	30.3	85.7	5.4E-04	2.4	Lower space velocity; next injection to ch
0.8	5.0	0.0	0.0	29.3	86.8	5.4E-04	2.4	after this run, cut off CO, flown H2 at 25
2.9	0.0	0.0	0.0	30.8	80.3	7.7E-04	7.9	Reaction started again on regenerated cata
1.8	0.9	3.4	0.0	34.7	83.5	8.2E-04	4.3	redn 50cc/min H2 350C(.5h
0.4	4.0	2.5	0.0	26.7	88.5	2.8E-03	2.2	Note selectivity changes
1.0	2.5	0.0	0.0	17.3	85.0	1.5E-03	1.3	End of reaction
0.0	0.0	0.0	0.0	70.5	37.1	2.2E-04	31.0	MeOH peak is only MeOH, no C3H8; area AcOH:
0.0	0.0	0.0	0.0	57.2	47.9	4.1E-04	32.8	End of reaction
0.0	0.0	0.0	0.0	65.3	39.5	2.2E-04	44.8	Rxn started at H2-20,CO-10 flow rates, but
0.0	0.0	0.0	0.0	70.7	40.4	1.2E-04	23.3	CO2 formation dropped drastically with tim
0.0	0.0	0.0	0.0	53.6	63.7	4.1E-04	21.7	Combined (AcOH+MeOAc) peak : ratio of AcOH
0.0	0.0	0.0	0.0	55.8	56.4	4.2E-04	21.9	
0.0	0.0	0.0	0.0	73.1	43.1	1.2E-04	18.0	
0.0	0.0	0.0	0.0	77.6	43.0	9.2E-05	20.2	CH4 area is not accurate
0.0	0.0	0.0	0.0	63.3	54.7	2.5E-04	23.9	End of reaction
5.7	0.0	0.0	0.0	35.6	50.6	6.6E-04	11.3	Combined (C3H8+MeOH) peak : 35% of C2H6 p
5.8	0.0	0.0	0.0	35.1	54.8	6.2E-04	11.0	Butane peak area - rough approximation ba
0.0	2.2	0.0	0.0	37.6	74.4	4.0E-04	3.0	Combined (AcOH+MeOAc) area : ratio of AcOH
0.3	1.9	0.0	0.0	25.3	73.2	1.4E-03	2.6	
0.0	2.9	0.0	0.0	18.3	82.6	2.1E-03	2.7	
0.0	4.2	0.0	0.0	24.6	83.3	1.6E-03	3.1	reaction continues
0.0	4.1	0.0	0.0	45.3	80.9	4.7E-04	2.6	
0.0	3.2	0.0	0.0	30.2	85.4	2.0E-04	1.8	End of the reaction
0.0	10.0	0.0	0.0	33.3	92.7	7.9E-04	10.3	redn 50cc/min H2 350C(.5hr),500C(1hr)
0.0	10.1	0.0	0.0	38.6	92.2	7.4E-04	7.3	areas of MeOH and MeOAc peaks corrected :
0.0	8.0	0.0	0.0	46.2	88.0	7.9E-04	5.0	propane area is 35% of that of ethane ar
0.0	2.5	0.0	0.0	43.8	86.6	6.6E-04	4.8	and the ratio of areas of AcOH and MeOAc i
0.0	0.0	0.0	0.0	48.6	84.6	7.1E-04	3.4	app. 1 to 1; these conclusions made by usi
0.0	0.0	0.0	0.0	54.7	84.2	4.7E-04	4.5	porapak T column later. Data typed 11/18/
3.3	4.5	0.0	0.0	31.3	83.8	5.5E-04	0.0	corrections made as follows: 30% of ? area
3.8	5.8	0.0	0.0	34.0	83.1	5.5E-04	0.0	rest MeOEt; No AcOH, all MeOAc; 2/3 of ar
4.1	3.0	0.0	0.0	36.1	75.8	4.8E-04	0.0	and rest is MeOH

KINETIC DATA

COMMENTS	HYDRO C% C1	c2	C3	c4	oxyg C% C1	C2	C3
area : 2/3 is propane, rest MeOH	56.0	2.9	5.7	2.4	3.9	28.9	0.0
t) area : 30% Butane, rest MeOEt	61.1	3.1	4.8	1.3	2.2	22.8	4.6
) area : all MeOAc, No acetic acid	62.2	2.7	3.0	0.9	1.9	25.2	4.1
	47.8	2.1	3.3	1.3	2.8	38.1	3.5
on as-recieved catalyst, dried.	43.4	2.4	1.0	0.0	12.7	38.7	1.8
2 flow at 300C for 2 hours	63.2	2.2	0.9	0.0	3.9	29.1	0.5
peak : 35% of C2H6 peak is propane, rest MeOH	60.8	1.9	0.8	0.0	5.4	30.3	0.6
) peak : approximate ratio = 1:1	54.3	1.6	0.7	0.0	9.0	34.0	0.3
	33.2	0.4	0.2	0.0	18.4	47.7	0.0
f the combined (C4H10+MeOEt) peak area	60.9	5.3	5.9	4.0	5.4	11.8	4.3
peak : 2/3 area is propane, rest MeOH	73.4	5.0	4.9	1.6	2.1	9.2	2.4
) peak : No AcOH, all MeOAc	63.0	5.2	6.2	1.6	2.5	15.1	2.7
evious condition	61.0	4.9	7.3	1.5	2.5	16.5	2.6
=1:2	67.8	4.1	5.0	1.4	2.6	14.1	2.5
	69.2	4.6	5.8	1.5	2.6	12.0	2.0
: lower than calculated area	76.8	4.7	5.3	1.1	2.0	7.4	1.1
1 50cc/min H2 350C(.5hr),500C(1hr)	66.8	5.2	5.8	1.5	2.4	14.2	2.3
	64.9	4.4	6.7	1.0	2.4	16.4	2.8
:.5hr,350 .5hr.500C 1hr	55.8	4.2	1.7	0.8	14.0	18.7	4.7
f C2H6 peak area;	55.7	5.3	2.2	0.0	6.1	28.5	2.1
peak : AcOH-MeOAc ratio is 1:1	68.5	5.1	2.6	0.6	3.7	17.9	0.9
approximation	71.0	6.2	3.1	1.4	2.7	14.3	0.8
dition	56.3	5.0	5.4	0.0	4.8	28.5	0.0
next injection to check reproducibility	58.4	6.1	4.2	1.1	4.3	26.0	0.0
ff CO, flown H2 at 250C, 450psi overnight	58.3	7.1	4.5	0.9	3.9	25.4	0.0
n on regenerated catalyst	57.6	5.5	5.2	1.0	6.1	20.9	3.8
50cc/min H2 350C(.5hr),500C(1hr)	54.9	4.9	4.3	1.2	5.7	23.3	2.3
[illegible]	62.4	5.6	3.5	1.1	3.1	19.4	1.7
	74.8	3.2	3.9	0.8	2.6	14.7	0.0
H, no C3H8; area AcOH:MeOAc = 1:1	29.5	0.0	0.0	0.0	44.4	26.1	[illegible]
	41.2	1.6	0.0	0.0	29.8	27.3	0.0
CO-10 flow rates, but cut down to half	31.9	2.7	0.0	0.0	39.5	25.8	0.0
drastically with time	29.3	0.0	0.0	0.0	42.2	28.6	0.0
peak : ratio of AcOH to MeOAc is 1:1	42.9	3.4	0.0	0.0	19.4	27.8	6.4
0	42.5	1.7	0.0	0.0	24.3	27.4	4.0
	26.9	0.0	0.0	0.0	41.6	31.4	0.0
ate	22.4	0.0	0.0	0.0	44.2	33.3	0.0
	32.8	4.0	0.0	0.0	28.6	34.5	0.0
k : 35% of C2H6 peak area is propane area	56.2	5.0	2.0	1.2	17.6	17.9	0.0
ugh approximation based on propane area	56.0	5.5	2.2	1.3	15.8	19.2	[illegible]
area : ratio of AcOH to MeOAc is 1:1	52.2	7.3	2.9	0.0	9.6	27.9	0.0
	66.4	5.4	2.2	0.7	6.8	17.4	1.1
	72.4	5.6	2.8	0.9	3.2	13.9	1.2
	65.3	6.5	2.7	0.9	4.1	19.6	[illegible]
	49.6	3.5	1.6	0.0	8.6	33.7	[illegible]
	66.4	2.5	0.9	0.0	4.4	25.8	[illegible]
.5hr),500C(1hr)	60.7	4.3	1.7	0.0	2.4	29.0	[illegible]
c peaks corrected :	55.8	4.0	1.6	0.0	3.0	33.1	[illegible]
that of ethane area	47.8	4.3	1.7	0.0	5.6	39.2	1.4
of AcOH and MeOAc is	49.8	4.4	2.0	0.0	5.9	35.4	[illegible]
nclusions made by using	51.4	0.0	0.0	0.0	7.5	38.6	[illegible]
r. Data typed 11/18/85	45.3	0.0	0.0	0.0	8.7	44.0	[illegible]
llows: 30% of ? area is butane,	56.0	3.3	7.2	2.3	5.1	21.6	[illegible]
ll MeOAc; 2/3 of area is C3H8	54.2	2.3	6.8	2.7	5.7	25.0	3.1
	50.9	2.4	7.7	2.9	8.7	24.2	3.0

TABLE II

KINETIC DATA

...NTS	HYDRO C% C1	c2	C3	c4	oxyg C% C1	C2	C3	C4	turnover no. sec-1
	56.0	2.9	5.7	2.4	3.9	28.9	0.0	0.0	7.87E-04
	61.1	3.1	4.8	1.3	2.2	22.8	4.6	0.0	2.00E-03
	62.2	2.7	3.0	0.9	1.9	25.2	4.1	0.0	1.40E-03
	47.8	2.1	3.3	1.3	2.8	38.1	3.5	0.0	1.48E-03
	43.4	2.4	1.0	0.0	12.7	38.7	1.8	0.0	5.81E-04
	63.2	2.2	0.9	0.0	3.9	29.1	0.5	0.0	9.24E-04
	60.8	1.9	0.8	0.0	5.4	30.3	0.6	0.0	8.39E-04
	54.3	1.6	0.7	0.0	9.0	34.0	0.3	0.0	1.08E-03
	33.2	0.4	0.2	0.0	18.4	47.7	0.0	0.0	3.21E-04
	60.9	5.3	5.9	4.0	5.4	11.8	4.3	0.0	2.95E-03
	73.4	5.0	4.9	1.6	2.1	9.2	2.4	0.6	8.15E-03
	63.0	5.2	6.2	1.6	2.5	15.1	2.7	2.6	5.20E-03
	61.0	4.9	7.3	1.5	2.5	16.5	2.6	1.2	3.47E-03
	67.8	4.1	5.0	1.4	2.6	14.1	2.5	0.6	4.92E-03
	69.2	4.6	5.8	1.5	2.6	12.0	2.0	0.7	6.19E-03
	76.8	4.7	5.3	1.1	2.0	7.4	1.1	0.3	1.12E-02
	66.8	5.2	5.8	1.5	2.4	14.2	2.3	0.6	4.85E-03
	64.9	4.4	6.7	1.0	2.4	16.4	2.8	0.4	3.39E-03
	55.8	4.2	1.7	0.8	14.0	18.7	4.7	0.0	1.23E-03
	55.7	5.3	2.2	0.0	6.1	28.5	2.1	0.0	9.87E-04
	68.5	5.1	2.6	0.6	3.7	17.9	0.9	0.8	3.21E-03
	71.0	6.2	3.1	1.4	2.7	14.3	0.8	0.0	4.86E-03
	56.3	5.0	5.4	0.0	4.8	28.5	0.0	0.0	8.96E-04
	58.4	6.1	4.2	1.1	4.3	26.0	0.0	0.0	8.55E-04
	58.3	7.1	4.5	0.9	3.9	25.4	0.0	0.0	8.54E-04
	57.6	5.5	5.2	1.0	6.1	20.9	3.8	0.0	1.22E-03
	54.9	4.9	4.3	1.2	5.7	23.3	2.3	3.4	1.31E-03
	62.4	5.6	3.5	1.1	3.1	19.4	1.7	2.5	4.48E-03
	74.8	3.2	3.9	0.8	2.6	14.7	0.0	0.0	2.40E-03
	29.5	0.0	0.0	0.0	44.4	26.1	0.0	0.0	4.11E-04
	41.2	1.6	0.0	0.0	29.8	27.3	0.0	0.0	7.79E-04
	31.9	2.7	0.0	0.0	39.5	25.8	0.0	0.0	3.50E-04
	29.3	0.0	0.0	0.0	42.2	28.6	0.0	0.0	1.87E-04
	42.9	3.4	0.0	0.0	19.4	27.8	6.4	0.0	6.52E-04
	42.5	1.7	0.0	0.0	24.3	27.4	4.0	0.0	6.67E-04
	26.9	0.0	0.0	0.0	41.6	31.4	0.0	0.0	1.88E-04
	22.4	0.0	0.0	0.0	44.2	33.3	0.0	0.0	1.46E-04
	32.8	4.0	0.0	0.0	28.6	34.5	0.0	0.0	3.96E-04
	56.2	5.0	2.0	1.2	17.6	17.9	0.0	0.0	1.15E-03
	56.0	5.5	2.2	1.3	15.8	19.2	0.0	0.0	1.07E-03
	52.2	7.3	2.9	0.0	9.6	27.9	0.0	0.0	6.87E-04
	66.4	5.4	2.2	0.7	6.8	17.4	1.1	0.0	2.37E-03
	72.4	5.6	2.8	0.9	3.2	13.9	1.2	0.0	3.59E-03
	65.3	6.5	2.7	0.9	4.1	19.6	0.9	0.0	2.70E-03
	49.6	3.5	1.6	0.0	8.6	33.7	2.9	0.0	8.13E-04
	66.4	2.5	0.9	0.0	4.4	25.8	0.0	0.0	3.53E-04
	60.7	4.3	1.7	0.0	2.4	29.0	1.8	0.0	6.80E-04
	55.8	4.0	1.6	0.0	3.0	33.1	2.4	0.0	6.45E-04
	47.8	4.3	1.7	0.0	5.6	39.2	1.4	0.0	6.86E-04
	49.8	4.4	2.0	0.0	5.9	35.4	2.5	0.0	5.72E-04
	51.4	0.0	0.0	0.0	7.5	38.6	2.4	0.0	6.17E-04
	45.3	0.0	0.0	0.0	8.7	44.0	2.0	0.0	4.05E-04
	56.0	3.3	7.2	2.3	5.1	21.6	4.5	0.0	2.48E-03
	54.2	2.3	6.8	2.7	5.7	25.0	3.1	0.0	2.48E-03
	50.9	2.4	7.7	2.9	8.7	24.2	3.0	0.0	2.18E-03

SELECTIVITY TO C2 OXYGENATES TABLE III

2%Na, 3% Rh/Alumina, at 450 psi (30 atmos.),275 C ,varied space rate.

% CO Conversion	12.8	6.1	3.2	1.8	1.5	0.8
Selectivity, % of CO Conversion						
acetaldehyde	6.3	9.4	12.4	13.6	15.8	19.8
ethanol	7.6	8.8	9.5	9.8	11.2	9.3
accetic acid	2.7	2.5	4.8	4.9	6.0	7.7
methyl acetate	2.5	2.3	4.5	4.6	5.7	7.3
ethyl acetate	10.0	10.1	8.0	2.5	0	0
selectivity to C2 oxygenates	29.1	33.1	39.2	35.4	38.7	44.1
selectivity to total oxygenates	33.3	38.6	46.2	43.8	48.8	54.7
selectivity of C2 oxygenates of total oxygenates	87	86	85	81	79	81

% CO conversion includes CO_2 formation.

% selectivities to oxygenates is on a CO_2 -free basis

For methly acetate, 2/3 has been counted as C2 oxygenate.

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