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Synthesis Gas Conversion over Supported Rhodium and Rhodium–Iron Catalysts

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When used as a catalyst for conversion of synthesis gas at pressures above 25 atm, supported rhodium produces two-carbon oxygen-containing compounds, specifically acetic acid, acetaldehyde, and ethanol, with chemical efficiencies on the order of 50%. The other major product is methane. These results are strikingly different from those obtained with other Group VIII metals and from those previously reported for rhodium. Reasons for the differences from earlier work are discussed. Addition of iron to the rhodium catalysts sharply reduces the yields of acetic acid and acetaldehyde. Ethanol becomes the principal two-carbon product and methanol appears as a major product. Hydrocarbon production remains low, at least up to an iron to rhodium mole ratio of unity.

INTRODUCTION

In recent years it has become amply evident that the petrochemical industry will have to consider alternatives to its traditional raw materials—ethane and other relatively light hydrocarbons obtained from natural gas or petroleum. Synthesis gas is obviously one such possibility, since it can be obtained from coal, residual oil, or waste products. Most of the extensive literature (*1*, *2*) on synthesis gas conversion is concerned with the catalytic production of hydrocarbons suitable for use as fuels. The catalysts most commonly used have been based on iron, cobalt, nickel, and ruthenium. Less information is available on the catalytic characteristics of the other Group VIII metals, although all have been investigated to some extent (*3–5*). A screening study of the lesser known metals of that group (*6*, *7*) gave evidence that rhodium had a unique ability selectively to produce two-carbon chemicals. Results obtained with supported Rh and Rh–Fe catalysts are presented and discussed here.

EXPERIMENTAL

Reaction system. Work was conducted in a flow system, with continuous feed of reactants metered by suitable orifices. The 1-liter Autoclave Engineers reactor was of the Berty back-mixed type described in Fig. 2 of Ref. (*8*). Products were recovered by partial condensation, followed by vapor phase chromatographic (vpc) analyses of the liquid and gaseous products. Feed gases were purified by passage over active carbon and/or Linde 13× molecular sieves. All equipment was of Type 316 stainless steel. The inside walls of the reactor and all internal parts exposed to the reacting gas mixture were plated with 0.0005 in. of gold or 0.001 in. of silver by Harper–Leader, Inc. This plating was applied because of evidence that $Fe(CO)_5$ and $Ni(CO_4)$ were being generated in the

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TABLE 1

Effects of Oxalic Acid-Washing of Davison Grade 59 Silica Gel

	Weight percentage of cation		
	Fe	Ca	Na
Before washing	0.024	0.054	0.085
After washing	0.010	0.015	0.002

reactor and that these were contaminating the catalysts under test. A variable-speed, magnetically driven fan continuously recirculated the reaction mixture over the catalyst bed. A brief study showed that, in operation at a pressure of 1000 psi, a fan speed of 800 rpm or higher gave maximum catalyst productivity. The following modifications were found to facilitate operation and to prevent runaway methanation reactions.

(1) Hydrogen feed gas was introduced continuously at the bottom of the autoclave through the well for the shaft of the Magnedrive agitator.

(2) Carbon monoxide feed gas was introduced continuously through a separate port at the bottom of the autoclave, in order to avoid a hydrogen-rich zone in the autoclave.

Experiments were conducted at 200 to 350°C and 25 to 200 atm of total pressure, with H_2:CO ratios ranging from 1:10 to 10:1. Gas hourly space velocities were varied from 500 to 50,000, typically being chosen to give synthesis gas conversions below 10%.

Description of VPC analytical methods. Liquid samples were analyzed for water, ethanol, acetic acid, methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, propionaldehyde, acetone, butyraldehyde, isopropanol, *n*-propanol, isobutanol, *n*-butanol, and amyl alcohol on a $\frac{3}{16}$ in. × 6 ft column of Porpak N. This column does not separate methanol and acetaldehyde. These were determined in a separate analysis on a $\frac{1}{8}$ in. × 22 ft column of 9% Silar 5CP on 30- to 80-mesh Haloport F. Two analytical procedures were performed on the uncondensed portion of the effluent gas stream at least once during the period of collection of each liquid sample. Hydrogen, carbon monoxide, and methane were determined using a $\frac{3}{16}$ in. × 8 ft column of charcoal modified with 1% Silicon QF-1. Methane, ethylene, ethane, propylene, propane, acetaldehyde, 1-butene, and *n*-butane were determined using a $\frac{1}{8}$ in. × 10 ft column of 50- to 80-mesh Porapak R.

Operating at conversion levels on the order of 1 to 2% puts considerable demands on the sensitivity of the analytical method when looking for products made at efficiencies of the order of a percent or less. It is probable that some minor products have been missed, but the principal products shown, made at carbon atom efficiencies of 5% or more, are thought to be well established. The trends of change in distribution with catalyst composition are more trustworthy than the absolute selectivity values reported.

Catalyst preparation. Catalysts were prepared by conventional incipient wetness techniques described in some detail in the issued patents (*6*, *7*). Rhodium was added as $RhCl_3 \cdot xH_2O$ and iron as $Fe(NO_3)_3 \cdot 9H_2O$. The support used in most of the experiments was 3- to 6-mesh Davison Grade 59 silica gel which had been washed with hot oxalic acid solution to remove cationic impurities. Typical analyses of this gel for iron, calcium, and sodium before and after washing are shown in Table 1. It has not been shown that oxalic acid washing produces any purer product than the more conventional nitric acid washing. Clearly even the washed silica gel is significantly contaminated with foreign ions. The gel particle size used was chosen to minimize mass transfer problems, based on theoretical analysis of the gel characteristics by standard techniques (*9*).

TABLE 2

Effects of Iron Additions on Selectivity[a]

Fe[b] (wt%)	CO conversion (%)	Efficiency (carbon atom percentage)							
		CH_4	Gas HC[c]	Total gas HC + oil	Methanol[d]	Ethanol[d]	Acetaldehyde	Acetic acid[d]	C_2 chemicals[e]
0.00	3.1	52.0	3.4	55.4	0.3	17.0	14.6	11.5	43.1
0.00	2.0	55.6	3.4	59.0	1.7	11.5	16.0	11.2	38.7
0.00	1.1[f]	50.7	3.2	53.5	1.5	15.9	15.5	12.2	43.6
0.05	3.5	49.0	2.2	52.5	2.8	31.4	4.2	9.1	44.7
0.10	4.2	49.6	1.6	51.2	5.6	33.6	2.6	6.5	42.7
0.20	3.3	42.1	1.1	44.2	21.1	29.2	0.5	4.0	33.7
0.50	1.8[f]	37.1	1.2	38.3	35.2	23.7	0.2	1.8	25.7
5.0[g]	4.8	24.6	43.8	76.9	9.4	4.0	7.6	0.0	11.6

[a] Activities and selectivities obtained in a silver-plated Berty-type, back-mixed reactor, with catalysts consisting of 2.5% Rh on oxalic acid-washed Davison Grade 59 silica gel, at 300°C, 1000 psig, 1:1 H_2:CO, and outlet gas flow rate of 18 g-mol/hr. Catalyst charge was 30 g $\simeq$ 75 cm^3 in all cases.

[b] Residual iron in the washed support $\simeq$ 0.01%.

[c] Gas HC includes all C_2–C_4 olefins and paraffins found.

[d] Including that which would be produced by hydrolysis of the esters produced.

[e] Defined as the sum of CH_3COOH, CH_3CHO, and C_2H_5OH.

[f] Used catalyst.

[g] No rhodium in this catalyst, only iron.

Other supports tested included porous silica beads (*10*), α- and γ-aluminas, and activated carbons. The most active catalysts were those prepared on silica gel and silica beads. γ-alumina always gave very inactive catalysts, possibly because of the difficulty with which rhodium on γ-Al_2O_3 is reduced to the metal (*11*). Metal dispersions on the supported catalysts were measured by CO chemisorption. This technique is now suspect in view of the evidence that an oxidized form of rhodium, presumably not a synthesis gas conversion catalyst, can absorb two CO molecules per rhodium atom (*11*). The dispersions measured by CO chemisorption on silica gel-supported catalysts were, however, in satisfactory agreement with the average metal crystallite sizes found by electron microscopy.

RESULTS

Data from tests of Rh/SiO_2 and Rh–Fe/SiO_2 catalysts are collected in Tables 2 and 3 and are shown graphically in Figs. 1 and 2. Figure 1 and Table 2 give data on CO conversion and on selectivities to the various products, measured at a standard set of operating conditions, for a series of catalysts with 2.5% Rh and varying amounts

TABLE 3

Effects of Iron Additions on Rates[a]

Fe[b] (wt%)	Initial Rh dispersion[c]	Rates (mole/kg/hr)		
		CH_4	CH_3OH[d]	C_2 chemicals[e]
0.00	35.4	5.46	0.04	2.29
0.05	30.9	5.75	0.26	2.63
0.10	29.6	6.01	0.59	2.67
0.20	NA	4.72	2.34	3.20
0.50	14.6	5.60	5.19	1.96[f]
5.0[g]	NA	4.36	1.60	0.89

[a] See Footnote *a* in Table 2.

[b] See Footnote *b* in Table 2.

[c] By Co chemisorption, assuming CO/Rh = 1 and CO/Fe = 0.

[d–g] See Footnote *d–g* in Table 2.

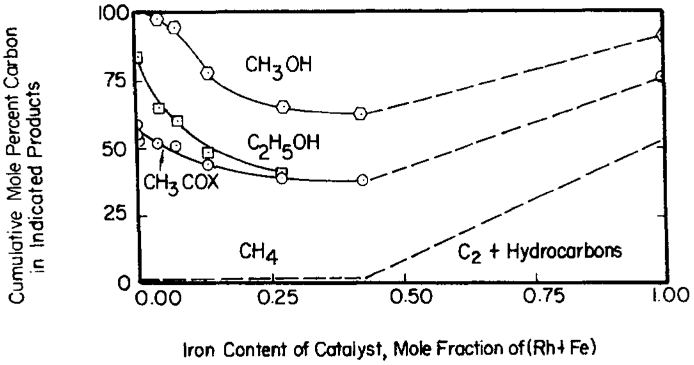

FIG. 1. Selectivities of rhodium–iron/silica gel catalysts.

of Fe on oxalic acid-washed silica gel. The same sort of data are also given for one catalyst which contained no Rh but simply 5% Fe on silica gel. Note that the iron contents of the catalysts are expressed as weight percentage of Fe in Tables 2 and 3, but as mole fraction of (Fe + Rh) in the related Figs. 1 and 2. Efficiency for the formation of the several products is expressed as carbon atom percentage of the total carbon appearing in products other than CO_2. CO_2 is omitted from the list of products for the purposes of this calculation since it and H_2O are more properly considered to be the two principal ways in which oxygen is removed from the CO when that is converted to CH_x groups not directly connected to oxygen. It can be argued that the carboxyl group in acetic acid represents another means of removing such oxygen. The approach described, which was originally developed for characterization of catalysts which produce hydrocarbons, was retained here. CH_3COX in Fig. 1 is the sum of the acetic acid plus acetaldehyde efficiencies.

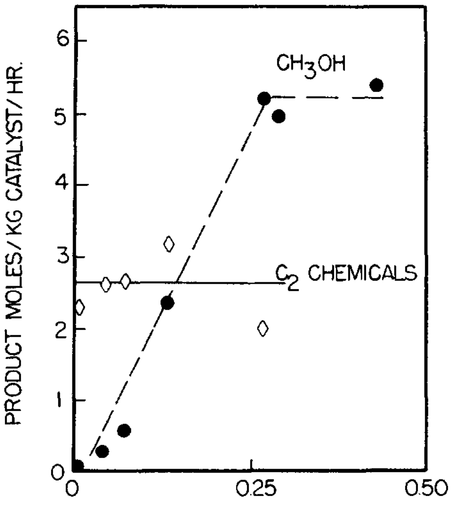

FIG. 2. Effects of iron on rates of product formation.

Figure 2 and Table 3 show data on rates to specific product groups for the same set of catalysts described in Fig. 1 and Table 2. Table 3 also gives the measured Rh dispersion on the unused catalysts after reduction at 500°C. The rates were measured after about 8–16 hr of operation in most cases. The catalyst containing 0.5% Fe was removed after one test run, then recharged because of uncertainties about the first results. The data available suggest that the CO conversion activity during the second run was somewhat lower than during the first. No major changes in activity or selectivity were noted, however.

The single product produced in greatest yield under the operating conditions shown was methane. The remainder was largely ethanol, acetaldehyde and acetic acid. No glycol was found. The product distributions obtained with rhodium and rhodium–

TABLE 4

Relative Effects of Changes in Operating Variables on Rates and Selectivities

	Rate			Efficiency		
	Temperature	pH_2	pCO	Temperature	pH_2	pCO
Acetic acid (CH_3COOH)	+[a]	+	0	−	−	+
Ethanol (C_2H_5OH)	++	++	−	++	+	−
Acetaldehyde (CH_3COH)	+	+	0	−−	−	+
Methane (CH_4)	+++	++	−	+++	++	−−−

[a] Effects are classified as negligible (0), small (+/−), moderate (++/−−), or large (+++/−−−). The + and − indicate whether the dependent variable increases or decreases on increasing the independent variable.

iron catalysts are dependent, *inter alia*, on the operating conditions—the temperature and the partial pressures of H_2 and CO in the reactor. Specifically, it can be shown that the ratio of methane to the C_2 oxygen-containing products obtained decreases as the H_2/CO ratio decreases. The relationship is not a simple linear one. Qualitative data on these effects are shown in Table 4. The effects reported were noted in experiments at 250 to 325°C, pressures ≥ 30 atm, and H_2:CO ratios ranging from 5:1 to 1:5. CO conversion was normally below 10%. A quantitative discussion, and the relation of the kinetics to the mechanism, are reported in another publication (*12*).

In Table 4, effects of the operating variables on the several rates and efficiencies cited are classified as negligible (0), small (+/−), moderate (++/−−), or large (+++/−−−). The + and − indicate whether the dependent variable increases or decreases on increasing the independent variable. Thus, increasing temperature increases all rates, but increases the rate of methane formation considerably more than the rate of acetic acid formation. On the other hand, raising the CO pressure—maintaining the other variables constant—decreases the efficiency of methane formation sharply while it increases the efficiency of formation of acetic acid and acetaldehyde.

The quantity of ethanol shown as being produced by the rhodium-only catalysts should be accepted with some reservations. Even when no iron was intentionally added during the catalyst preparation, traces of iron or nickel could have found their way to the catalyst surface by the time the test was completed. In addition to the 0.01% Fe known to be in the support, data were later obtained which showed that gold plating could actually contribute to nickel contamination of the catalyst, in tests similar to those described here. This occurs because a thin layer of nickel must be applied before gold is plated on stainless steel, in order to insure adhesion of the coating. Any porosity of the gold deposit then can result in the generation of nickel carbonyl in the reactor during testing. Tests not described here were run on catalysts to which small amounts of nickel had been added. These showed that, while traces of methanol were made by catalysts containing nickel, nickel was much less effective than iron in causing methanol and ethanol formation.

DISCUSSION

Earlier studies on the use of rhodium as a synthesis gas conversion catalyst, either as rhodium black or supported on carriers, give no evidence of high selectivity to two-carbon chemicals. Representative results

TABLE 5

Comparision of Experimental Results: Rhodium-Catalyzed Conversion of Synthesis Gas

Author	Year	Temperature (°C)	Pressure (atm)	pH_2/pCO	RGV[a]	HAc + EtOH + HOAc (mole%)
Fischer *et al.* (*3*)	1935	300–400	1	5	0.24	None found
Kratel (*13*)	1937	195	100	2	~1.3	Presume like Soufi
Eidus *et al.* (*14*)	1965	250–300	1–40	2–1	2.2 to 5.4	Presume like Soufi
Shultz *et al.* (*4*)	1967	441	20	3	60	None found
Soufi (*15*)	1969	140–220	220–1000	2	0 to ~0.2	0.14–3.37
This study		200–350	25–250	0.1–10	~10 to 2000	>50

[a] Relative gas velocity. As used here, the relative gas velocity is the volume of synthesis gas, measured in liters at 1 atm and 0°C, fed to the catalyst per gram of rhodium present per hour.

available from the literature are summarized in Table 5. From the work by Fischer *et al.* (*3*), Shultz *et al.* (*4*), and Vannice (*5*), it is well established that rhodium at atmospheric pressure is a moderately active methanation catalyst. No oxygen-containing products were detected. Kratel (*13*), Eidus *et al.* (*14*), and Soufi (*15*) carried out their studies at pressures of 40 atm and higher. They obtained liquid products. Pichler (*16*) described Kratel's products as "in addition to liquid and gaseous hydrocarbons, including the widest variety of oxygen-containing compounds."

The most detailed prior study of rhodium catalysts for the conversion of synthesis gas at elevated pressures is that by Soufi (*15*). Table 6 presents a comparison of results reported by Soufi at one set of conditions (Expt. D) with results obtained in this work under somewhat different conditions (Expts. A, B, and C). Our own results were obtained early in this investigation, at a time when techniques were not strictly comparable to those used in generating the data collected in Table 2. Furthermore, our results were obtained using diverse catalyst formulations and different test reactors, which may account for some of the differences shown. Nevertheless, Expt A gave results not greatly different from those reported in Table 2 for an iron-free catalyst, with whatever differences there are being in the direction to be expected as a result of the difference in operating pressure. Experiments B and

TABLE 6

Effects of Temperature and Conversion

Experiment	Temperature (°C)	CO conversion (%)	Carbon efficiency to product (%)[a]						
			CH_4	C_2H_6[b]	Oil	C_2H_5OH	CH_3CHO	Higher aldehydes	CH_3COOH
A[c]	300	1.4	42	—	0	8	18	3	22
B	200	5.0	28	—	27	3	18	2	22
C	300	41	27	25	16	3	12	4	11
D (Soufi)	200	50	8	19	48[d]	0.4	0	20	1

[a] C_3^+ acids and alcohols were found in amounts ≤3% carbon efficiency.

[b] Significant only if present.

[c] (A) 5% Rh/α-Al_2O_3; (B) 5% Rh/SiO_2; (C) 1% Rh/α-Al_2O_3; (D) Rh black. Pressure in A, B, and C = 170 atm; in D, 230 atm.

[d] Includes C_3^+ hydrocarbons.

C show that decreasing temperature or increasing conversion resulted in increased ethane and oil formation. Soufi's reaction conditions (230 atm, 8.5-hr residence time) could not conveniently be duplicated in the equipment used in this study, so it is only possible to infer what might have been the result of doing so. It does seem possible that the combination of low temperature and high conversion would have resulted in the high yields of higher hydrocarbons he reported in this and other experiments. His use of low flow or static reaction systems would tend to exaggerate the observed effects of high conversion.

Other possible explanations for the differences between Soufi's results and those reported here, including possible effects of iron and of added water, were considered and rejected. Soufi found relatively high yields of higher aldehydes, which would have disappeared if iron contamination had been a problem. No effect of adding water was noted in either study. Soufi did mention that feeding aldehydes to his reaction system resulted in the formation of hydrocarbons. Feeding of acetaldehyde to the systems used here, during synthesis, failed to cause any increase in methane formation, though hydrogenation and aldol condensation did occur.

Turning now to the effects observed when iron was added purposely during the catalyst preparation in order to produce Rh–Fe/SiO_2 catalysts, it is apparent from Tables 2 and 3 that the methane selectivity dropped slightly and the spectrum of oxygen-containing products shifted toward the alcohols with increasing iron content. At 0.5% Fe, production of acetaldehyde and acetic acid had virtually stopped. Ethanol became the principal C_2 chemical produced, and methanol became a major product. There still was very little hydrocarbon or higher alcohol production (<3%), and no glycol formation. CO_2 was produced in significant quantities only by the catalysts containing iron. The 5% Fe/SiO_2 catalyst was relatively inactive and its selectivity for higher hydrocarbon

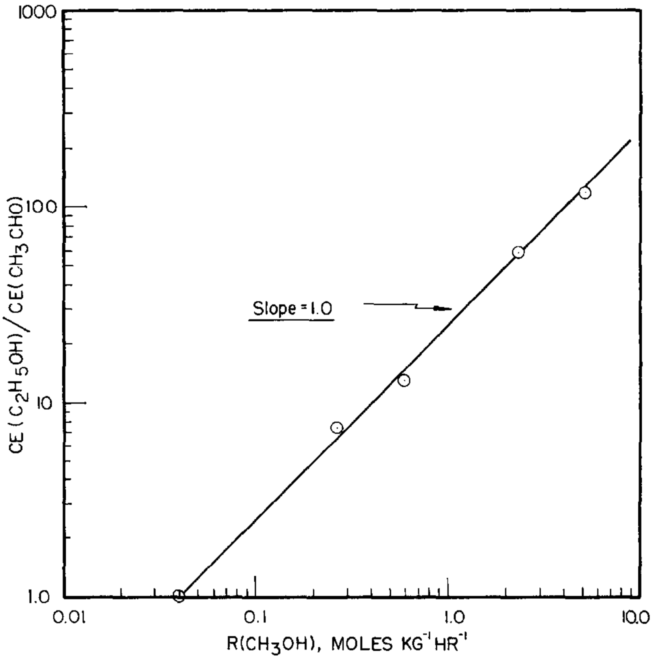

FIG. 3. Relationship of methanol and ethanol rates of formation.

production was much more characteristic of the iron-based catalysts described in the literature (*17*, *18*)—something over 50 carbon atom% of the CO converted to products other than CO_2 going to C_2+ hydrocarbons.

One correlation of the product distribution and rate data presented in Tables 2 and 3 is worthy of special note. Figure 3 is a plot of the rate of methanol formation in moles per kilogram per hour (Table 3) versus the ratio of ethanol to acetaldehyde production efficiency (Table 2) for the whole range of Fe contents investigated with Rh-containing catalysts. There is a direct proportionality between the two sets of numbers over a range of two orders of magnitude. The $CE(C_2H_5OH)/CE(CH_3CHO)$ ratio is proportional to the rate constant for the hydrogenation of acetaldehyde, since the rate of that reaction is proportional (*19*) to the acetaldehyde partial pressure (concentration) in the back-mixed reactor, and the H_2 and CO concentrations did not differ significantly in the experiments reported. The relationship of this rate constant to the rate of methanol formation raises the possibility that the methanol is being formed by hydrogenation of formaldehyde on the same sites. Thermodynamic equilibrium limits the formaldehyde concentration in the liquid products of these experiments to $\leq 0.5\%$ (*20*), a quantity which would not be detected by the analytical methods employed. The data in Fig. 3 would be reasonable, though, if formaldehyde were made rapidly enough to reach its equilibrium concentration. Then that concentration would be roughly the same in all the products. With a constant formaldehyde concentration, the rate constant for its hydrogenation to methanol could be proportional to the measured rate of methanol formation.

Extension of the work of Garten and Ollis (*21*) on the Pd–Fe system to the Rh–Fe system discussed here would lead to the expectation that the Fe should become associated with the Rh metal crystallites present. If so, the presence of Fe on the Rh surface has no appreciable influence on the rate of CH_4 or C_2 chemical production. The effects of Fe observed in this investigation could equally well be a result of its forming separate aldehyde hydrogenation sites, perhaps by interaction with the silica support, leaving the Rh crystallite surface unchanged from that generated in Rh/SiO_2 catalysts.

In conclusion and in summary, it has been shown that rhodium, when operated at low conversions and at pressures above atmospheric, pressure, converts synthesis gas to C_2 chemicals with selectivities not previously possible. Additions of small quantities of iron to supported rhodium catalysts cause major shifts in the catalyst selectivity pattern. Selectivity to methane drops somewhat and that to acetaldehyde and acetic acid almost disappears. The major C_2 chemical made by catalysts containing 0.2 to 0.5% Fe is ethanol. Methanol is produced by those catalysts in quantities comparable to those of methane and ethanol.

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