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Synthesis Gas: A Raw Material for Industrial Chemicals

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Summary. Rapid increases in the price of imported crude oil have accelerated a shift in the raw material base for chemical feedstocks from natural gas to crude oil to coal. Widespread use of ethylene as a feedstock has depended on the availability at attractive prices of natural gas and petroleum. As the resource base shifts from natural gas and petroleum to coal, ethylene is being replaced by synthesis gas (a mixture of hydrogen and carbon monoxide of varying composition), which can be manufactured directly from any of these carbonaceous sources. This trend is expected to accelerate in the 1980's. Organics likely to be produced from synthesis gas include ethanol, ethylene glycol, and vinyl acetate.

The critical elements for chemical (and fuel) feedstocks are carbon and hydrogen. Over the years, the source of these elements has changed, reflecting availability and price. Fifty years ago coal was the resource base for most chemicals, including ammonia, benzene, toluene, xylene, naphthalene, methanol, and glycol. In more recent years, the three major resources have been natural gas, crude oil, and coal. This sequence—gas, crude, coal—represents an order of increasing processing difficulty. The current widespread use of ethylene as a chemical building block is due largely to the ease with which ethane is abstracted from abundant natural-gas liquids and cracked to ethylene.

As we approached the 1960's, the availability of natural gas began to decline and oil was imported from the Middle East in large quantities and at attractive prices. A shift toward naphtha as a source of chemical feedstock then began, even though this presented problems in selective carbon and hydrogen (C, H) utilization. For example, full-range naphtha cracking produces about 30 percent ethylene (*1*), compared to up to 85 percent from ethane. But large amounts of propylene, butadiene, and aromatics are coproduced, and thus the derivatization and marketing of these coproducts became an important part of petrochemical economics. The growth of the propylene-based industry during the 1960's and early 1970's was due largely to the plentiful supply generated by the shift to heavier feedstocks.

The rapid increase in price of Mideast oil, which began in the early 1970's and is continuing, has again turned attention to the plentiful, but refractory, raw material coal. Coal use presents a new set of problems: the H/C ratio is not as favorable as that in natural gas or petroleum, the mining and subsequent handling of solids are more difficult mechanically, and large amounts of ashing minerals are sometimes present. From a chemical point of view, one of the most severe problems is the inability to crack coal directly to ethylene and other desirable light olefins.

In any of the areas discussed above, synthesis gas—a mixture of hydrogen and carbon monoxide in varying proportions—plays an important role. Since synthesis gas can be made from nearly any source of carbon, it is becoming the raw material of choice when derived from fossil fractions less amenable to conventional processing. In the United States for many years synthesis gas was made by reforming of methane (for example, natural gas)

$$CH_4 + H_2O \rightleftarrows CO + 3\ H_2 \text{ (endothermic)} \qquad (1)$$

Starting with this primary reaction, ammonia, urea, and methanol could be manufactured with very attractive economics. Because of this, synthesis gas is currently manufactured in huge quantities—7×10^{10} pounds a year, compared to 2.4×10^{10} pounds a year for ethylene (*2, 3*).

As the availability of methane continues to decline and petroleum fractions become scarce and more expensive, it becomes increasingly desirable to produce synthesis gas from "the bottom of the barrel." Partial oxidation of increasingly heavy petroleum fractions is receiving more attention (*4*)

$$\left.\begin{array}{l} C_mH_{2n} + \frac{m}{2}O_2 \rightarrow mCO + nH_2 \\ C_mH_{2n} + mH_2O \rightarrow mCO + (m+n)H_2 \end{array}\right\} \qquad (2)$$

A typical vacuum residuum has a viscosity of 120 to 300 centistokes at 160°C, a pour point of 60° to 85°C, a sulfur content of 6.0 percent by weight, and a vanadium and nickel content of 140 parts per million. The synthesis gas produced has an H_2/CO ratio slightly less than 1.0, compared to 3.0 from methane reforming and 1.8 from partial oxidation of methane (*5*). A sour (high-sulfur) heavy residuum has been reported (*5*) as the C, H source for a joint venture of DuPont and U.S. Industrial Chemicals which is starting up this year (*6*).

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Coal as a Source of Chemicals

As an energy source, coal can be utilized in three ways: by direct combustion to generate heat, conversion to clean liquid products for fuel, and gasification to methane. The last reaction, discovered by Sabatier and Senderens in 1902 (*7*)

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

was the basis for later research on coal that resulted in the Fischer-Tropsch reaction, in which higher hydrocarbons are produced from carbon monoxide and hydrogen (*8*). This reaction is basically deficient in energy conservation, since the reaction of coal with water is highly endothermic and proceeds at relatively high temperatures, whereas the formation of methane is highly exothermic at the relatively low temperatures of 300° to 350°C.

The Fischer-Tropsch reaction was extensively researched during the period 1925 to 1945. In 1936 the first commercial plant was put into operation by Ruhrchemie; it was based on a heterogeneous Co-ThO_2-MgO-kieselguhr (diatomite) catalyst (*9*). This catalyst and variations on it were used extensively by Germany during World War II to produce necessities ranging from gasoline to synthetic fats. After the 1940's, the availability of Mideast oil ended commercial development of the process, except in South Africa. In that country, the availability of large deposits of coal that could be mined at low cost and the inaccessibility of external supplies of crude oil resulted in the construction of the Sasol I complex. Sasol I produces nearly 250,000 tons of primary products a year with two types of reactors, both of which use iron-based Fischer-Tropsch catalysts. One produces a C_5^+ product of 32 percent gasoline, 21 percent diesel fuel, and 47 percent higher paraffins. The second produces nearly 70 percent gasoline-range fuel (*9, 10*). Sasol II, which is nearing completion, has been designed to employ 36 gasifiers and produce annually 1.5 million metric tons of fuel products, 150,000 metric tons of ethylene, 100,000 metric tons of ammonia, and 200,000 metric tons of coal-tar derivatives (*11*).

It is evident that the commercial experience gained during decades of use makes the Fischer-Tropsch process one of the first methods to consider for the production of organic chemicals from coal via synthesis gas. However, the indiscriminate nature of the product formation presents a very discouraging picture to a manufacturer who wishes to build a new plant to produce, for example, ethylene or *n*-butanol. The only chemical produced singly with high efficiency directly from synthesis gas is methanol. As we will discuss later, the mechanism for methanol formation over catalysts based on copper (I) oxide and zinc oxide bears a close resemblance to that for Fischer-Tropsch or other carbon monoxide–hydrogen reactions according to some proposed schemes, but not according to others.

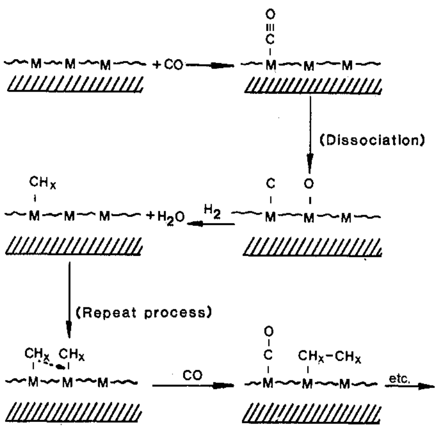


Fig. 1. Possible mechanism of Fischer-Tropsch chain growth; *M* is a metal and *x* = 1 or 2.

Methanol as an Intermediate

Since the processes for making methanol are very selective and commercially proved and synthesis gas from any C, H source is acceptable, many routes to hydrocarbon fuels and chemicals are expected to proceed through this simple intermediate. (This is in addition to the utility of methanol itself as a primary fuel.) An outstanding technology of this type is that developed by researchers at Mobil Oil (*12*). Shape-selective zeolites produce hydrocarbon materials from methanol that are predominately in the gasoline range and have both aromatic and aliphatic components. More of the higher octane gasoline blending stocks are produced than by the Fischer-Tropsch process.

The shape-selective zeolites are intermediate in pore dimension between the familiar wide-pore faujasites and the very narrow-pore zeolites such as zeolite A. It is pore dimension that controls product distribution. A typical product distribution obtained with shape-selective zeolites, expressed as percent by weight of the total hydrocarbon fraction, is: (aliphatic) C_4, 26; C_5, 10; C_6^+, 4; and (aromatic) benzene, xylenes, trimethylbenzenes, and tetramethylbenzenes, 41. Mobil Oil's process has been adopted in New Zealand for gasoline production. Synthesis gas can be readily obtained from the Maui natural gas field (*13*).

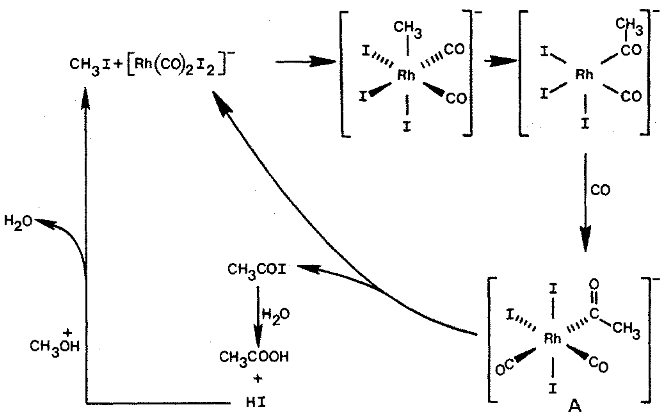
In addition to gasoline, olefins such as ethylene and propylene can be produced under selected conditions (*14*). Workers in Europe are also studying zeolite-type catalysts for producing lower olefins (*15*). The multitude of new opportunities for methanol in the production of fuels and chemicals should make it an increasingly important commodity chemical.

Homogeneous versus Heterogeneous Reaction

Up to this point, the discussion has centered around the increasing motivation for use of synthesis gas as a raw material. The reactions involved may also be examined in terms of heterogeneous versus homogeneous catalysis. A heterogeneous catalyzed reaction is understood here as one in which a solid insoluble catalyst interacts with gaseous or liquid reactants and products. A homogeneous catalyzed reaction is one having a soluble catalyst in a solution with liquid or dissolved gaseous reactants and products (*16*). The recent advent of metal carbonyl cluster complexes, pioneered by Chini (*17*), has led to the intriguing possibility that soluble clusters may behave, on a localized basis, like metal surfaces with chemisorbed species (*18, 19*).

Speculations about the mechanisms of cluster catalysis revived a theory of Fischer-Tropsch hydrocarbon synthesis that is as old as the reaction itself—namely, that the reaction proceeds through intermediate formation of surface metal carbides (*20*–*22*). This is supported by use of ^{13}C-labeled carbon monoxide (*22*), infrared spectral examination of reacting surfaces (*23*), hydrogenation of accumulated surface carbon several monolayers thick (*22, 23*), and the correlation between the ability of a metal to dissociate carbon monoxide and its Fischer-Tropsch reactivity (*21*). It has been concluded that the metals most active in Fischer-Tropsch hydrocarbon synthesis are those that form metal carbides and metal oxides of intermediate stability (*21*). Also, it has long been recognized that chain growth in Fischer-Tropsch synthesis resembles a polymerization reaction, with chain initiation, chain propagation, and chain termination steps (*24*). The picture that emerges as quite likely, on the basis of current knowledge, is shown in Fig. 1.

A valid sequence such as that involving carbon monoxide dissociation would explain the paucity of examples of homogeneous Fischer-Tropsch analogs



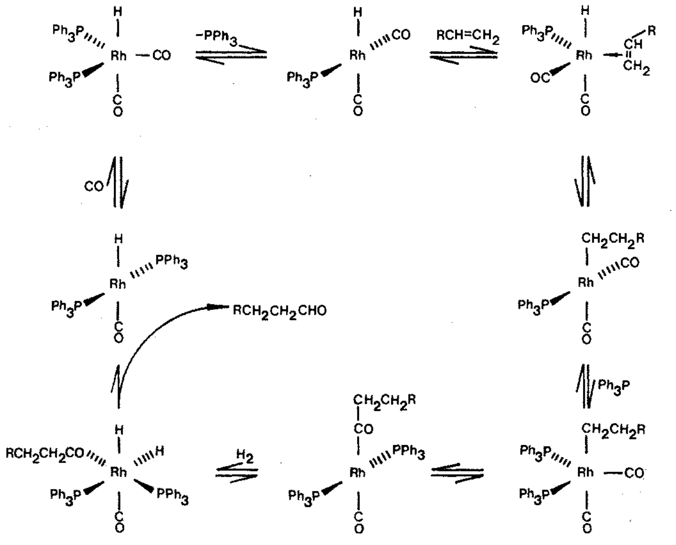


Fig. 2 (left). Catalytic cycle for the conversion of methanol to acetic acid with a rhodium-methyl iodide catalyst. Fig. 3 (right). Mechanism of reaction 10 for complex A and linear isomer formation.

(*25*, *26*). In fact, the direct synthesis of methanol, ethylene glycol, glycerine, and higher polyols from synthesis gas (*27-31*) has been termed the nearest analog to Fischer-Tropsch synthesis (*32*). In this unusual catalytic reaction, the carbon-oxygen bond is retained during the growth sequence.

A dramatic example of homogeneous versus heterogeneous catalysis was given by Bradley (*33*) and by Doyle *et al.* (*34*), who showed that soluble ruthenium (carbonyl) produced methanol from carbon monoxide and hydrogen, whereas heterogeneous, cluster-derived ruthenium produced Fischer-Tropsch reactions. These results provide additional evidence that in carbon monoxide chemistry homogeneous and heterogeneous systems may act in fundamentally different ways.

Homogeneous Catalytic Systems

The rest of this article will focus primarily on homogeneous catalytic systems and their present or potential impact. It is interesting to note that one of the first metal carbonyl-catalyzed reactions of synthesis gas, the oxo process, was derived from studies of the heterogeneous Fischer-Tropsch synthesis route. Homogeneous catalysis has certain inherent advantages: it is more amenable to direct study; a continuum of reactivity patterns can be achieved through incremental alterations of ligands; there is high selectivity of products; and heat removal is easy for highly exothermic reactions and isothermal reaction conditions. Use of some or all of these advantages in synthesis gas chemistry has resulted in dramatic changes in manufacturing processes during the past decade, and all indications are that this trend will continue.

Two particular cases are the manufacture of acetic acid and of *n*-butanol. In the late 1950's, when ethylene could be obtained relatively inexpensively from natural gas liquids and light naphtha, a new process was instituted for its homogeneous oxidation to acetaldehyde. The acetaldehyde was oxidized to acetic acid

$$CH_2{=}CH_2 + \frac{1}{2}\,O_2 \xrightarrow[Cu^{2+}]{Pd^{2+}} CH_3CHO \qquad (4)$$

and this became one of the principal routes to acetic acid.

Meanwhile, Imperial Chemical Industries perfected a low-pressure (750 to 1500 pounds per square inch) process for converting synthesis gas to methanol. In the late 1960's, Monsanto researchers found a novel method for carbonylating methanol to acetic acid with very high selectivity—more than 99 percent (*35-37*)—over a catalyst consisting of a combination of soluble rhodium species and methyl iodide. The rhodium concentration is approximately 10^{-3} molar and the reaction conditions are ~ 180°C and 30 to 40 atmospheres (carbon monoxide and autogenous pressure of organic compound). The kinetic influences are particularly interesting. None of the reactants

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (5)$$

or products in Eq. 5 enters into the kinetic expression for reaction rate. The rate has first-order dependences on rhodium and iodide promoter concentrations only (*35-38*). The reaction is also catalyzed by cobalt and iodide and by iridium and iodide. The former method was commercialized by BASF in 1965 (*39*) but requires higher pressures (500 to 700 atm) and is less selective for acetic acid (90 percent). The latter is effective at relatively low pressures but has more complicated kinetics (*40*). The rhodium-catalyzed process was commercialized in 1970, and when plants under construction worldwide are completed, it will produce nearly one-third of all the acetic acid manufactured (*37*).

The catalytic cycle is shown in Fig. 2 and its mechanism has received much attention (*35-38*, *40*). The "active species" is $[Rh(CO)_2I_2]^-$. The cycle contains the mechanistic elements of oxidative addition, carbonyl insertion (or methyl migration), and reductive elimination. Oxidative addition of methyl iodide to the rhodium(I) species is the rate-determining step.

The second case is that of butanol. When ethylene was inexpensive and readily available from natural gas or light naphtha, the commercial process of choice was based on acetaldehyde

$$CH_2{=}CH_2 \rightarrow CH_3CHO \qquad (6)$$

$$2\,CH_3CHO \xrightarrow{(aldol)} \left[CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2CHO \right] \rightarrow CH_3CH{=}CHCHO \qquad (7)$$

$$CH_3CH{=}CHCHO \xrightarrow{H_2} CH_3CH_2CH_2CHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH \qquad (8)$$

The process was utilized for butanol as the marketed chemical product, or for butyraldehyde (Eq. 8) as an intermediate in the manufacture of 2-ethylhexanol. The latter compound has been a mainstay alcohol for esterification with phthalic anhydride to produce di(2-ethylhexyl) phthalate, a leading plasticizer for vinyl resins.

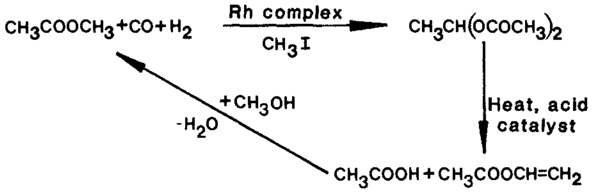


Fig. 4. Production of vinyl acetate from methyl acetate and synthesis gas.

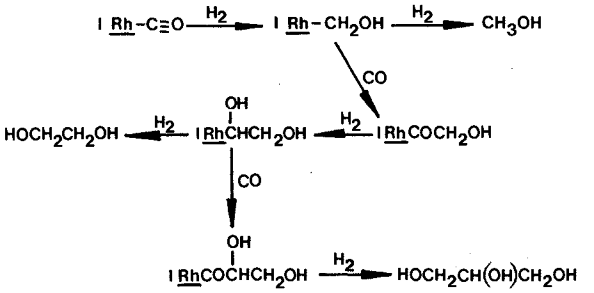
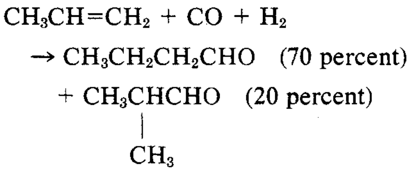


Fig. 5. Possible mechanism of polyhydroxylic alcohol synthesis over rhodium catalyst.

Once again, the change in feedstock economics has resulted in a change in the method of manufacture. Propylene became increasingly available as heavier feedstocks were cracked to obtain ethylene. Synthesis gas was available from a variety of sources, principally associated with ammonia and methanol manufacture. In fact, the CO/H_2 ratio of the product from partial oxidation of higher petroleum fractions is 0.9/1.0 to 1.2/1.0 (5). A ratio of 1/1 is ideally suited for the oxo reaction, as shown in Eq. 9



$$\mathrm{CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO}\ \text{(70 percent)} + \mathrm{\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCHO}}\ \text{(20 percent)} \quad (9)$$

The oxo process gained prominence during the1950's, even though the overall efficiency for the desired *n*-butyraldehyde was low (65 to 70 percent); alcohol, alkane, and aldol by-products complicated the processing, high pressures (250 to 350 atm) were required, and the cobalt hydrocarbonyl catalyst was unstable, volatile, and difficult to maintain in a catalytic cycle.

The deficiencies of the cobalt oxo process became more critical as raw materials became more expensive and as the cost impact of its energy requirements rose rapidly. In 1976 the low-pressure, rhodium-catalyzed oxo processes became a commercial reality (27, 41-44) and provided a satisfactory solution to all the problems cited above. Chemical efficiencies of producing the desired *n*-butyraldehyde are greater than 90 percent (less than 8 percent *iso* aldehyde), there is negligible by-product formation, the required pressures are low (200 to 400 psi), and a stable, nonvolatile catalyst system is used [$HRh(CO)_n(PPh_3)_{4-n}$ where $n = 1$ or 2 and PPh_3 is triphenylphosphine]. Since its initial commercialization, the process had been licensed for nine plants in seven countries (45). The homogeneous catalyst in solution is probably A or B (or both) in the equilibrium

$$\mathrm{HRh(CO)_3PPh_3 \underset{CO}{\overset{PPh_3}{\rightleftharpoons}} \underset{A}{HRh(CO)_2(PPh_3)_2} \underset{CO}{\overset{PPh_3}{\rightleftharpoons}} \underset{B}{HRh(CO)(PPh_3)_3}} \quad (10)$$

The mechanism (46) involves phosphine and olefin complexation, olefin and carbonyl insertion, oxidative addition, and reductive elimination, as illustrated in Fig. 3 for complex A and only linear isomer formation.

Because of the favorable economics in these two examples, synthesis gas chemistry is entering into the manufacture of certain oxygenated compounds. The acetic acid technology replaced ethylene feedstock with feedstocks that can be derived from heavy oil fractions or from coal.

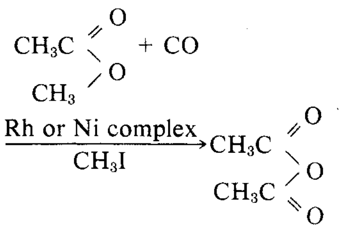
$$\mathrm{CH_2{=}CH_2 \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH}$$
$$\mathrm{CO + 2\,H_2 \rightarrow CH_3OH \xrightarrow{CO} CH_3COOH} \quad (11)$$

The oxo technology replaces ethylene with the propylene by-product from cracking the heavy petroleum fraction and with synthesis gas.

$$\mathrm{CH_2{=}CH_2 \xrightarrow{[O]} CH_3CHO \rightarrow CH_3CH{=}CHCHO \rightarrow CH_3CH_2CH_2CHO}$$
$$\mathrm{CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO} \quad (12)$$

Processes for the 1980's

A dramatic entry into the technology of the 1980's has been made by Tennessee Eastman, which has announced a plant for converting coal to synthesis gas to acetic anhydride (47-50). This provides a direct link between coal as the ultimate fossil C, H source and a downstream product. The technology has not been described but has been publicized as a combined technology of Eastman Kodak and Halcon International [for example, see (45)]. The patent literature reveals that methyl acetate can be carbonylated to acetic anhydride with carbon monoxide in the presence of group VIII metals and iodide (51-54).



$$\mathrm{CH_3C(=O)OCH_3 + CO \xrightarrow[CH_3I]{Rh\ or\ Ni\ complex} CH_3C(=O){-}O{-}C(=O)CH_3} \quad (13)$$

The acetic anhydride product can result from reaction with acetyl iodide in an anhydrous medium (55) (see also Fig. 2) or from the interaction of complex A (Fig. 2) with acetic acid.

$$\mathrm{\underset{A}{[Rh(CO)_2(COCH_3)I_3]^-} + CH_3COOH \rightarrow [Rh(CO)_2I_2]^- + (CH_3CO)_2O + HI} \quad (14)$$

It was disclosed earlier by Monsanto scientists that methanol carbonylation can give methyl acetate (37); this completes the linkage between the product anhydride and synthesis gas.

Public speculations (49) and the patent literature (56) suggest that this type of technology may be applied in the future to produce vinyl acetate through ethylidene diacetate (Fig. 4).

Polyhydroxylic alcohol synthesis. Rhodium-catalyzed synthesis of polyhydroxylic compounds directly from CO and H_2 has been under study by workers at Union Carbide for several years (27-30)

$$\mathrm{CO + H_2 \xrightarrow[bases]{Rh\ catalyst} CH_3OH + HOCH_2(CHOH)_{\mathit{x}}CH_2OH} \quad (15)$$

where $x = 0, 1, 2, \ldots$ This unique reaction has attracted much attention because of its relatively high specificity for ethylene glycol, an important commodity chemical. This selectivity is due to (i) the unusual type of catalysis, which is superficially related to a homogeneous system for alcohols and to Fischer-Tropsch C-C building, and (ii) the fact that carbonyl complex clusters are present under reaction conditions. It has been stated that this is the first homogeneous synthesis of methanol (*57*) in addition to ethylene glycol.

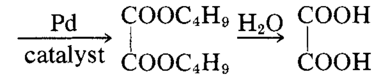
The catalyst system for polyhydroxylic alcohol production includes a soluble anionic rhodium carbonyl complex, which under reaction conditions consists largely of rhodium cluster carbonyls ranging up to at least Rh_{13} (*30*). This has generated speculation that the multinuclear complexes may resemble a metal surface and thus be a type of "homogeneous-heterogeneous" catalyst. However, the mobility of the clusters in solution and the observation of mononuclear tetracarbonylrhodate anion preclude any definite assignment of the catalytically active species.

The mechanism of formation is not known. It has been suggested that the reaction proceeds through a hydroxymethyl rhodium species (*27, 31*), where the rhodium may be either a portion of a cluster or a mononuclear carbonyl (Fig. 5).

Because the reaction takes place at a high pressure and temperature and requires a comparatively high concentration of rhodium, it has been difficult to define a commercial process based on this interesting reaction. News reports (*58*) have alluded to a new low-pressure (less than 1000 psi) process for ethylene glycol from synthesis gas that yields 80 to 95 percent glycol and does not use a noble metal catalyst. No further details of this process have appeared, but it would appear to be extremely attractive.

Other possibilities. Ube Industries in Japan has opened a plant for producing oxalic acid (*59*).

$2\,C_4H_9OH + 2\,CO + 1/2\,O_2$



$$\xrightarrow[\text{catalyst}]{\text{Pd}} \begin{array}{c} COOC_4H_9 \\ | \\ COOC_4H_9 \end{array} \xrightarrow{H_2O} \begin{array}{c} COOH \\ | \\ COOH \end{array} \qquad (16)$$

It is interesting that hydrogenation of the intermediate dibutyl oxalate would produce ethylene glycol and regenerate the starting butanol; the net reaction would produce glycol from synthesis gas.

$$2\,CO + 4\,H_2 + 1/2\,O_2 \rightarrow HOCH_2CH_2OH + H_2O \qquad (17)$$

The so-called homologation reaction, or the production of ethanol from methanol, has been known for nearly three decades. The term homologation describes the net growth of the alcohol by one CH_2 group.

$$CH_3OH + CO + 2\,H_2 \rightarrow CH_3CH_2OH + H_2O \qquad (18)$$

As first reported (*60*), the reaction was catalyzed by a cobalt carbonyl species. However, yields were low (42 percent ethanol) and there was a spectrum of by-products, including acetaldehyde, methyl formate, methyl acetate, propanol, butanol, and methane.

Ethanol is being introduced for use as transportation fuel in order to extend petroleum supplies. The fuel is either 100 percent ethanol, as in Brazil (*61*), or a blend containing ethanol, such as gasohol in the United States. The ethanol is produced by grain fermentation, even though the energy balance for this source has been questioned (*62*). The potential for this chemical is enormous, both for fuel and as a potential source of ethylene, the olefin with the largest volume and value. It is clear that synthesis gas from coal must be considered for ethanol production, either directly or through methanol.

Because of this potential, there has been much activity in the chemistry of ethanol production from CO and H_2 in the last few years. The homologation reaction has been reinvestigated and selectivities from methanol to ethanol of more than 80 percent have been claimed (*57*). The best homogeneous catalysts to date contain ruthenium and iodide ion in addition to cobalt and may contain phosphorus ligands (*63*).

Processes for making ethanol directly from synthesis gas by use of heterogeneous catalysts have also been disclosed (*64–67*). Some of these catalysts contain rhodium and produce a range of C_1 to C_4 linear alcohols, with an ethanol content of 40 to 60 percent. Of special interest is the product spectrum obtained with a cobalt-copper-chromium-potassium catalyst (*67*), which consists of methanol, ethanol, *n*-propanol, and *n*-butanol with proportions by weight (in one example) of 0.61, 1.00, 0.56, and 0.44 and only minor amounts of branched-chain alcohols or nonhydroxylic compounds. It has been claimed (*68*) that mixtures of C_1 to C_6 alcohols have beneficial properties in a gasoline mixture with aromatic or paraffinic hydrocarbons. Such concepts indicate that alcohols, particularly methanol and ethanol, will become increasingly important as both fuels and chemical feedstocks.

The swing to heavier feedstocks, including coal, presents great challenges and opportunities for CO and H_2 chemistry and for heterogeneous and homogeneous catalysis. The advances made in homogeneous processes for organic oxygenate intermediates have depended on raw material versatility, process efficiency, selectivity for the desired product, and mild reaction conditions. As processes are adapted and perfected according to the needs and circumstances of different industrial clients, the total base of technology will continue to broaden. The introduction of materials derived from synthesis gas (methanol, ethanol, methyl *t*-butyl ether, and so on) into the fuel industry in units of barrels per day rather than pounds per year will be slower to materialize, but their impact will be great. It will be fascinating to observe the changes over the next two decades.

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Impact on Agriculture of the Mount St. Helens Eruptions

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Summary. Ash from Mount St. Helens has fallen over a diverse agricultural area, with deposits of up to 30 kilograms per square meter. Crop losses in eastern Washington are estimated at about $100 million in 1980—about 7 percent of the normal crop value in the affected area and less than was expected initially. Production of wheat, potatoes, and apples will be normal or above normal because the favorable conditions for growth of these crops since the ashfall helped offset the losses. Alfalfa hay was severely lodged under the weight of the ash, but ash-contaminated hay is apparently nontoxic when eaten by livestock. The ash as an abrasive is lethal to certain insects, such as bees and grasshoppers, but populations are recovering. The ash has increased crop production costs by necessitating machinery repairs and increased tillage. On soil, the ash reduces water infiltration, increases surface albedo, and may continue to affect water runoff, erosion, evaporation, and soil temperature even when tilled into the soil. Ash on plant leaves reduced photosynthesis by up to 90 percent. Most plants have tended to shed the ash. With the possible exception of sulfur, the elements in the ash are either unavailable or present in very low concentrations; and no significant contribution to the nutrient status of soils is expected.

The massive volcanic eruption on 18 May 1980 of Mount St. Helens in the southwestern corner of Washington State destroyed life and property to the north, west, and east as far away as 20 to 25 kilometers. In addition, an estimated 1.5 to 2.0 cubic kilometers of ash fell on farm, range, and forest land reaching almost to the Dakotas on the east and into Canada on the north (*1*). Montana and a small part of Canada received only a light dusting, but agricultural areas in east-central Washington and adjacent northern Idaho received the ash in amounts up to 300 metric tons per hectare (Fig. 1A). An estimated 49 percent of Washington State received visible ash and 29 percent of the state received deposits of 3 millimeters or more (*2*). The heaviest deposits in Washington formed a layer 5 to 8 centimeters deep on the soil (Fig. 1C), with isolated cropland areas reporting uncompacted ash up to 15 centimeters deep. Rain beginning a few days later compacted the ash to about one-third the initial depth.

The affected area in eastern Washington consists mainly of eight counties (Fig. 1B), which, in 1979, accounted for $1.4 billion of crops and $270 million of livestock and livestock products. These values were 65 and 38 percent, respectively, of the total state crop and livestock production. The major crops include tree fruits (32,000 ha), hay (153,000 ha), potatoes (24,000 ha), cereal grains (964,000 ha), and dry edible legumes (100,000 ha). Minor ones include mint, hops, vegetable seed, and other specialty crops. The region includes a major portion of the irrigated Columbia Basin, a large dryland wheat-fallow area, and a dryland area that is cropped annually (Fig. 1).

Ash from the eruptions of 25 May and 12 June fell in southwest Washington and northwest Oregon, including farmland in the Willamette Valley, but rarely produced an uncompacted layer more than 1 cm thick. The ash from the 22 July eruption drifted northeast along the eastern edge of the Cascade range, producing a layer of ash up to 3 mm deep in northeastern Washington and light dusting into Canada.

Volcanic activity has been considerable in the northwest United States and the provinces of adjacent Canada during the past several thousand years, and the material discharged is believed to have been blown easterly about 80 percent of the time (*3*). Compared with the cumulative deposits of loess and ash to date, the soil material provided by the recent eruptions of Mount St. Helens is almost insignificant. On the other hand, these are the first volcanic eruptions to occur in the area since agriculture of any consequence began there and are probably the most massive volcanic eruptions to directly affect a temperate region of wide-scale and intensive agriculture.

The full impact of the eruptions on the soils and on the plant and animal life where ash fell will never be known and even now is mostly speculation. Initial estimates that losses to crops and livestock would be large have been revised

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