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# Carbon monoxide: feedstock for chemicals, present and future

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The chemistry of carbon monoxide has attracted academic and industrial interest since its discovery. Hardly any other molecule has challenged the imagination of theoretical, preparative and industrial chemists more.

In 1903, Sabatier pioneered the hydrogenation of carbon monoxide, which should become a very important reaction in industry. Furthermore, his mechanistic proposals are milestones in the development of heterogenous catalysis.

The Boudouard and water gas shift reaction are early examples of industrial carbon monoxide applications. Also the reactions of carbon monoxide with other reagents exemplified in eq. 1–5 have a long history.

$$CO + Cl_2 \longrightarrow COCl_2 \qquad (1)$$

$$CO + S \longrightarrow COS \qquad (2)$$

$$4CO + Ni \longrightarrow Ni(CO)_4 \qquad (3)$$

$$CO + NH_3 \longrightarrow HCN, HCONH_2 \qquad (4)$$

$$CO + CH_3OH \longrightarrow HCOOCH_3 \qquad (5)$$

Many of these reactions are still practiced today and often represent well established processes.

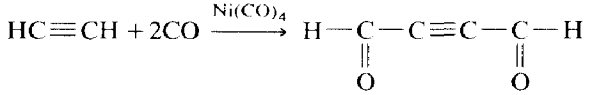
In 1925, Fischer and Tropsch succeeded in converting synthesis gas into mixtures of liquid oxygenates and hydrocarbons. The first plant applying this discovery was built in 1934 by Ruhrchemie. Others followed bringing the production in a short time to 400000 tons per year. Today Fischer–Tropsch technology is used only in South Africa. In today's economics, giving product distribution and energy requirements, this process is less attractive than crude oil processing, but Fischer–Tropsch chemistry could become important again with future oil shortages.

At BASF Mittasch's discovery in 1913 of the hydrogenation of carbon monoxide to methanol was exploited by building the first commercial plant in 1924. A zinc-copper catalyst was used in the Leuna plant. Methanol and higher alcohols were produced by a technique of synthesis turning away from the destructive distillation of wood, which had been applied since the seventeenth century. Mittasch's invention still is the best process for the manufacture of methanol. Catalyst improvements and plant design changes characterize the development from 1913 to today. Recently, it has been demonstrated that soluble Ni salts can be used in a homogeneous process. However, the formation of $Ni(CO)_4$ proves bothersome and it must be seen whether this route can compete with the well optimized heterogeneous process.

The beginning of industrial homogeneous transition metal based catalysis can be attributed to the work of Reppe at BASF in the early thirties. At this time acetylene was the main raw material for the German chemical industry. It was made by a reaction shown in eq. 6.

$$\begin{aligned} CaO + 3C &\longrightarrow CaC_2 + CO \\ CaC_2 + H_2O &\longrightarrow Ca(OH)_2 + CH{\equiv}CH \end{aligned} \tag{6}$$

In this reaction one mole of CO and one mole of acetylene are formed. The carbon monoxide being burned bothered the industrial chemist Reppe who tried to convert it according to eq. 7 to $C_4$-units, which could be used for butadiene production.



$$HC{\equiv}CH + 2CO \xrightarrow{Ni(CO)_4} H{-}\underset{\underset{O}{\|}}{C}{-}C{\equiv}C{-}\underset{\underset{O}{\|}}{C}{-}H$$

However, the reaction followed another pathway (eq. 8) giving acrylic acid due to water present. This finding led to a series of carbonylation processes at BASF (IG-Farben) utilized for the production of acids or esters according to eq. 8–10.

$$CH{\equiv}CH + CO + H_2O(ROH) \xrightarrow{Ni(CO)_4} CH_2{\equiv}CH{-}COOH \text{ (ester)} \tag{8}$$

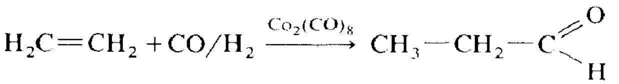
$$CH_2{=}CH_2 + CO + H_2O(ROH) \xrightarrow{Ni(CO)_4} CH_3{-}CH_2{-}COOH \text{ (ester)} \tag{9}$$

$$CH_3OH + CO \xrightarrow{Co_2(CO)_8} \text{acetic acid} \tag{10}$$

Only in recent years has the production of acrylic acid been altered by a feedstock change to propylene oxidation. The production of acetic acid via methanol carbonylation still represents the best technological way for its synthesis. The use of rhodium by Monsanto instead of cobalt marks a major break-through.

In this connection another industrial achievement applying carbonylation chemistry must be mentioned. Tennessee Eastman is producing acetic anhydride from syn-gas. The overall process starts from coal which is converted to syn-gas. The latter is used for methyl acetate synthesis via methanol carbonylation to acetic acid followed by esterification. The $[Rh(CO)_2I_2]^-$ catalyzed carbonylation of methyl acetate yields acetic anhydride. This carbonylation route will replace more and more the conventional acetic anhydride manufacture via acetic acid pyrolysis.

The use of hydrogen plus carbon monoxide (eq. 11) was never reported by Reppe.



(11)

In 1938, Roelen discovered this reaction which today is better known as hydroformylation. Olefins in the $C_3$–$C_{20}$ range are used to make aldehydes, alcohols and acids. With more than 6 million t produced per year, this is one of the most important reactions in industry. The most frequently applied starting olefin is propene which amounts to close to 50%.

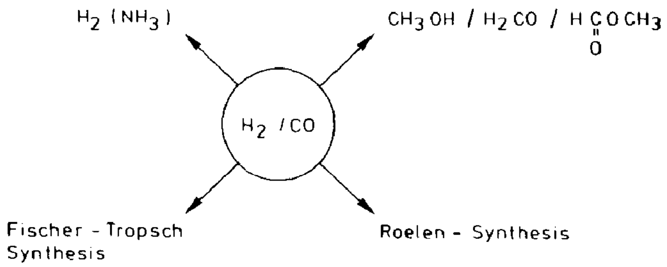


Fig. 1.

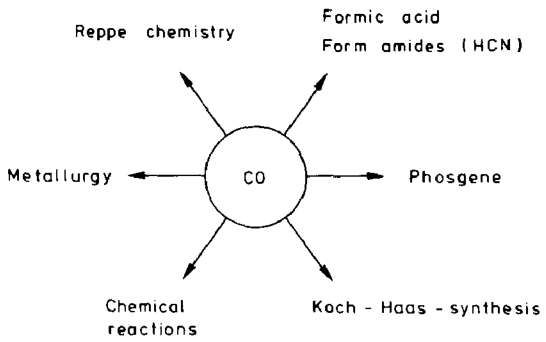


Fig. 2.

From an industrial point of view, the syn-gas chemistry is most important. Fig. 1 exhibits the major industrial applications.

Syn-gas is the major source for hydrogen production which is needed for ammonia synthesis. Methanol is used for formaldehyde production.

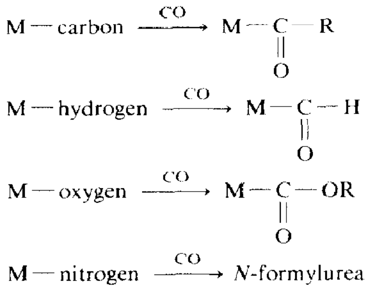
The use of pure carbon monoxide is much less attractive on a cost basis than $CO/H_2$. This is mainly due to the separation costs associated with low temperature distillation or copper-salt complexation, which both are applied in CO manufacture. Therefore, whenever possible the chemist in industry will use syn-gas instead of pure CO. However, there are various processes which are based on pure carbon monoxide and which are listed in Fig. 2.

## Future of carbon monoxide chemistry

Carbon monoxide can be synthesized from practically any carbon source (see Fig. 4). For the conversion of synthesis gas to useful industrial products homogeneous and heterogeneous catalysis will be applied. The use of homogeneous transition metal catalysis in syngas chemistry can be seen for various reasons:

> Homogeneous catalysts often show significant advantages in selectivity, activity and ease of modification. Since a key factor in synthesis gas chemistry is better selectivity, homogeneous systems could play an important role. Homogeneous reactions occur under rather mild reaction conditions, thus offering economic benefits in the saving of energy.

The hydrogenation of CO is exothermic and heterogeneous systems are plagued



$$\mathrm{M{-}carbon} \xrightarrow{\mathrm{CO}} \mathrm{M{-}\underset{\underset{O}{\|}}{C}{-}R}$$

$$\mathrm{M{-}hydrogen} \xrightarrow{\mathrm{CO}} \mathrm{M{-}\underset{\underset{O}{\|}}{C}{-}H}$$

$$\mathrm{M{-}oxygen} \xrightarrow{\mathrm{CO}} \mathrm{M{-}\underset{\underset{O}{\|}}{C}{-}OR}$$

$$\mathrm{M{-}nitrogen} \xrightarrow{\mathrm{CO}} N\text{-formylurea}$$

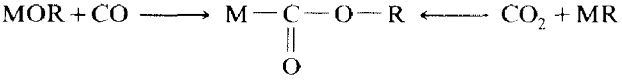
Fig. 3. CO insertion reactions (M = metal).

by problems of heat removal. Homogeneous systems operating in the liquid phase offer advantages.

Homogeneous transition metal catalysts, in a broad sense, are offsprings of organometallic complex chemistry. Here complexes and reactions with CO and $H_2$ are among the most studied areas. A wealth of information and understanding is available providing the nutrient of applications. It may be generalized: the better our fundamental understanding the better are the chances of finding applications.

Organometallic chemistry has provided a good understanding of CO insertions and some examples are shown in Fig. 3.

These insertions lead to C–C coupled products and to compounds containing a functional group. Both are essential and crucial steps in making industrially useful products. A reaction less well studied is the CO insertion into a metal–oxygen bond, which links carbon monoxide with carbon dioxide chemistry as exhibited in eq. 12.



$$\mathrm{MOR + CO \longrightarrow M{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longleftarrow CO_2 + MR} \tag{12}$$

This could become important because $CO_2$ is an abundant raw material and its manufacture is associated with the water gas shift reaction in providing hydrogen. Synthesis gas offers many routes to industrial chemicals. They can be classified in a direct and an indirect path as shown in Fig. 4.

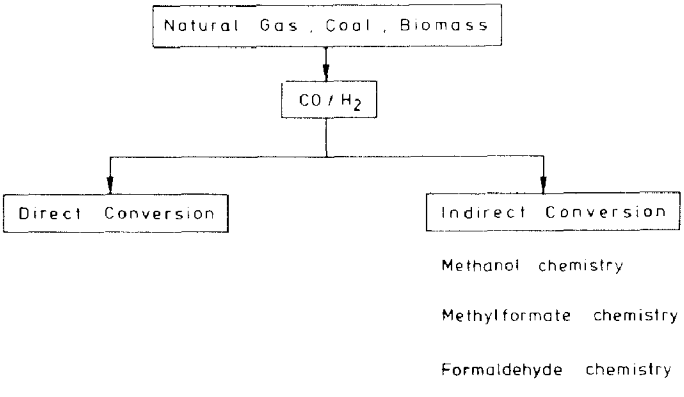


Fig. 4.

The direct conversion deals with the straight hydrogenation of carbon monoxide to paraffins, olefins and heteroatom (oxygen, nitrogen) containing products. The indirect conversion invokes intermediates such as methanol, methyl formate and formaldehyde. The latter ones in a consecutive reaction can yield a variety of desired chemicals. For instance, acetic acid can be synthesized directly from $CO/H_2$, but for reasons of selectivity the carbonylation of methanol is by far the better process.

The direct conversion is well known as the Fischer–Tropsch reaction yielding mixtures of mainly linear alkanes and/or alkenes. There have been many attempts to tailor the product slate to $C_2/C_3$ olefins only. However, all data indicate that the Schulz–Flory selectivity dominates. Mechanistically, the Fischer–Tropsch synthesis can be described by a geometric progression (Schulz–Flory distribution) in which the chain growth probability can possess various values. Prior to entering a costly research and development program, simple calculation can help to evaluate whether the mathematically determined product distribution can be balanced economically on the market. Tailoring the product distribution (selectivity) remains a challenging goal. Some research groups attack this problem by catalyst modifications. Other attempts aim at product adjustments by employing addition processes. Thus Shell has released details of its new process to transform natural gas to middle distillates, such as naptha, gasoil and kerosene. In this scheme, methane is first converted to $CO/H_2$ followed by a Fischer–Tropsch type reaction using a proprietary catalyst. To adjust the product distribution the paraffins are hydrocracked to produce middle distillate.

Based on economics the formation of oxygenates retaining at least one of the oxygen atoms of the original CO reactant is favoured. Potential applications exist here for the direct synthesis of alcohols, acids and esters. Methanol is by far the most promising chemical manufactured already from $CO/H_2$ in many millions of tons. The higher alcohols such as ethanol and propanol are potential candidates for chemicals of gasoline usage, alone or blended. Therefore many companies in different countries are working on the synthesis of oxygenates.

In our laboratory we are investigating the direct hydrogenation of CO to isobutanol as it was practiced by BASF and still is done in the German Democratic Republic. We have developed catalysts which yield isobutanol in selectivities between 50–60% at good $CO/H_2$ conversions. Isobutanol can be used as feedstock for isobutene (chemical usage) or can be converted with methanol to MTBE (fuel usage).

Most remarkable is the high pressure, rhodium catalyzed homogeneous reduction of carbon monoxide to ethylene glycol pioneered by Union Carbide. The great technical potential of this process is obvious when considering the poor selectivity with which ethylene glycol is currently manufactured from ethene. From a technical point of view, however, the rhodium catalyzed synthesis of ethylene glycol possesses various disadvantages: First of all, the high pressure being necessary for reasonable activities and selectivities has to be mentioned. (Here recent results from Japan showing a pressure range between 300–400 bar are encouraging). A very expensive metal, rhodium, is used. Catalyst recycle and circumvention of any rhodium loss will be difficult. The manufacture fibre grade ethylene glycol the purification cost will be high. Various attempts have been made to use a less costly metal and/or to lower the pressure, but a breakthrough has not been reported, so far. It appears, that from

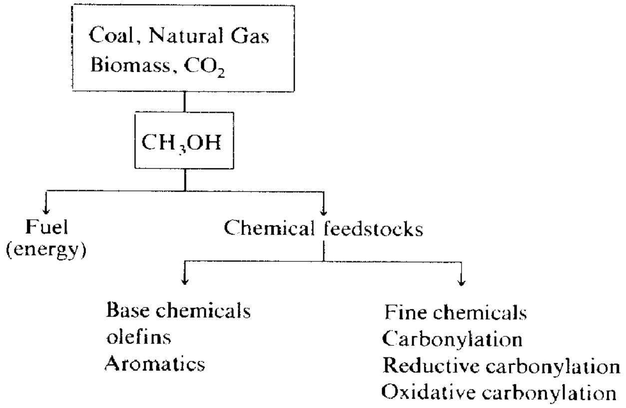


Fig. 5.

all the metals tested, rhodium possesses the highest activity and selectivity followed by cobalt and ruthenium.

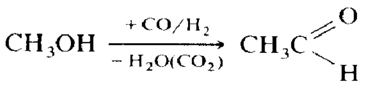
As is outlined in Fig. 4, the indirect path using methanol, formaldehyde or methyl formate as intermediates can be used for the synthesis of chemicals from synthesis gas. Here methanol serves greatest attention. It can be used directly as fuel or converted via Mobil technology into gasoline (Fig. 5).

Many reactions are known which use methanol also for the synthesis of base chemicals as well as fine chemicals. Again via Mobil technology using ZSM-5 type zeolites, olefins and aromatics can be manufactured.

For the synthesis of fine chemicals, carbonylation, reductive carbonylation, and oxidative carbonylation of methanol can be applied. While the direct carbonylation is well accepted by industry, the reductive and oxidative carbonylations are still in the research and development stage. The oxidative coupling of CO in the presence of an alcohol to yield oxalate esters is under study by Ube Industries and Union Carbide. In a subsequent reaction, the oxalate can be hydrogenated to ethylene glycol. Oxalate esters can also be treated with $NH_3$ giving oxamides, a fertilizer.

The oxidative carbonylation of methanol to dimethyl carbonate has found already some industrial application.

In our laboratory substantial effort was devoted to study of the homologation of methanol to acetaldehyde (eq. 13).



$$CH_3OH \xrightarrow[-H_2O(CO_2)]{+CO/H_2} CH_3CHO \qquad (13)$$

A catalyst system $[(Ph_3P)_2N][Co(CO)_4]/I_2$ in the presence of a polar solvent, such as sulfolane or dioxane yielded at 97% methanol conversions, 80% selectivities to acetaldehyde at rates of 1250 $h^{-1}$. In cooperation with Union Rheinische Braunkohlen Kraftstoff AG, Wesseling a pilot plant was operated over 3 years. The data obtained and the results of the catalyst recycle look very promising for a commercial operation. An engineering evaluation led to the following conclusions: In comparison to the Wacker process, the homologation of methanol is the more economical process. However, the costs of construction don't justify closedown economics for Wacker plants. In addition, due to the Monsanto process, which displaces the acetaldehyde oxidation to acetic acid, there is currently no need for a

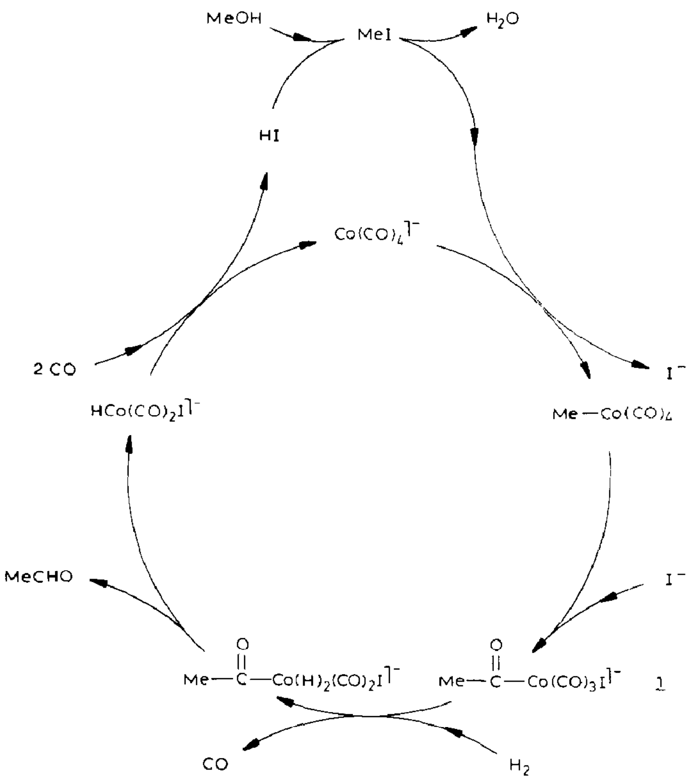
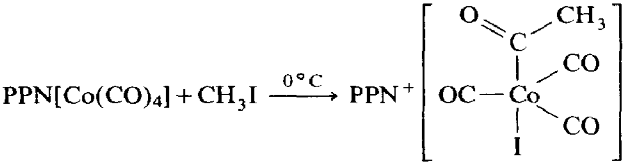


Fig. 6.

new acetaldehyde plant. However, the author is convinced that the next acetaldehyde plant will be based on methanol homologation.

Detailed investigations were also carried out in our laboratory to understand the reaction mechanism. Based on kinetics and reactions with model complexes, the mechanism of Fig. 6 is proposed.

In a separate cycle methanol reacts with HI yielding methyl iodide, which alkylates $[Co(CO)_3]^-[(Ph_3P)_2N]$ yielding complex **1**. Hydrogenation of **1** gives acetaldehyde. Coordination of CO closes the catalytic cycle via elimination of HI and return to $[Co(CO)_3]^-$. Kinetic measurements support that the alkylation of the cobalt complex with methyl iodide is the rate-determining step. Indeed, addition of $CH_3I$ to a solution of $[(Ph_3P)_2N][Co(CO)_4]$ at 0 °C gives the novel anionic complex **1** (eq. 14).



$$PPN[Co(CO)_4] + CH_3I \xrightarrow{0\,°C} PPN^+ \quad (14)$$

**1**

Complex **1** has a trigonal bipyramidal structure with three equivalent carbonyl ligands as could be confirmed by X-ray analysis. The synthesis of complex **1**

Table 1

Combination of crude oil derivatives with syngas

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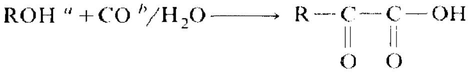
Hydroformylation

$C_4H_6$ [a] $+ 2CO$ [b] $+ 2CH_3OH$ [b] $\longrightarrow$ adipic acid

$C_6H_5NH_2$ [a] $+ CO$ [b] $+ CH_3CH_2OH$ [b] $\xrightarrow{O_2}$ $C_6H_5NHCO_2CH_2CH_3 + H_2O$ isocyanates

bisphenol A [a] $+ CO/O_2$ [b] $\longrightarrow$ polycarbonate

toluene [a] $+ CO$ [b]$/HBF_4$ $\longrightarrow$ terephthalic acid



$ROH$ [a] $+ CO$ [b]$/H_2O \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH$

$n\ CH_2{=}CH_2$ [a] $+ m\ CO$ [b] $\longrightarrow$ polyketones

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[a] Oil derived. [b] Derived from alternative resources.

depends on the solvent and cation used. The chemical reactions of **1** are also in agreement with the proposed mechanism. Reaction with $Ph_3P$ yields $Co(CO)_3[C(O)CH_3]Ph_3P$. Addition of hydrogen leads to acetaldehyde.

As outlined, based on syn-gas, direct and indirect paths are available to prepare a variety of chemicals or fuel. The chemical industry has been always tied to the energy providing industry. This also will be true in the future. Developments in the fuel market will govern the development of chemicals. Therefore the cost of crude oil is most crucial. However, even with low crude oil prices, we cannot afford to neglect research and developments in the field of CO chemistry. Long range syn-gas chemistry will come, only the timetable is unknown. Researchers particular in the academic world should continue to study carbon monoxide chemistry. One day it will be needed and then we must have it available.

It is reasonable to assume that prior to the exclusive use of chemicals derived from feedstocks other than crude oil, chemicals based on crude oil and chemicals based on alternate feedstocks will supplement each other. This situation has already arisen as is exemplified in the use of coal derived $CO/H_2$ to hydroformylate olefins originating from mineral oil. For instance, in West Germany Hoechst converts coal into $CO/H_2$ which is used to prepare alcohols from naphtha derived olefins. Table 1 summarizes a number of additional reactions which are under investigation and in which this point is especially emphasized.

Predicting the future is difficult. One should never forget: "The only certainty about the future is uncertainty".

## References

1 J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, Weinheim, 1980.

2 D.R. Fahey (Ed.), Industrial Chemicals via $C_1$ Processes, ACS Symposium Series 328, American Chemical Society, Washington, 1987.

3 F. Asinger, Methanol — Chemie- und Energierohstoff, Springer Verlag, Weinheim, 1986.

4 R.G. Herman (Ed.), Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals, Plenum Press, New York, 1983.

5 R.A. Sheldon, Chemicals from Synthesis Gas, D. Reidel Publishing Company, Dordrecht, 1983.

6 D.M. Bibby, C.D. Chang, R.F. Howe, S. Yurchak (Eds.), Methane Conversions, Elsevier, Amsterdam, 1988.
7 G. Henrici-Olivé, S. Olivé, Catalyzed Hydrogenation of Carbon Monoxide, Springer Verlag, Weinheim, 1984.
8 W. Keim (Ed.), Catalysis in $C_1$ Chemistry, D. Reidel Publishing Company, Dordrecht, 1983.