# INTRODUCTION

Carbon monoxide has gained steady importance in chemical industries as a cheap raw material for the syntheses of various compounds since 1855 when Berthelot discovered the reaction between carbon monoxide and caustic alkali leading to the synthesis of formates. The importance of carbon monoxide has become well evident during the last thirty years and a number of new reactions of carbon monoxide of immense industrial potentialities have been discovered where it combines with another organic reagent, entering the molecule of the organic compound in the form of carbonyl group and through this way aldehydes, ketones, acids, esters etc. are produced.

A thorough literature survey reveals that the reactions of carbon monoxide under high pressure leading to the syntheses of various organic compounds can be categorised as (i) reactions with hydrogen; (ii) reactions with alcohols; (iii) reactions with olefins or olefinic compounds and water or compounds containing active hydrogen atom;[1] (iv) reactions with acetylene and water or other compounds containing active hydrogen atoms; (v) reactions with aldehydes or ketones and water or alcohols; (vi) reactions with ethers; (vii) reactions with primary, secondary and other amines; (viii) reactions in which carbon monoxide acts as a reducing agent; (ix) reactions with organo-metallic compounds and (x) reactions with alkyl or aryl halides and water or alcohols[2].

(i) The reactions of carbon monoxide and hydrogen lead to the synthesis of various hydrocarbons (Fischer Tropsch synthesis), methanol, higher alcohols and various other compounds when the reaction conditions such as pressure, temperature catalysts etc. are changed. Generally the oxides or the reduced metals of transition group elements (either supported or unsupported) are employed as catalysts.

(ii) The direction of reaction of carbon monoxide with alcohol depends to a considerable extent on the nature of the catalyst. Formates or higher carboxylic acids or their esters may be the reaction products. The acid catalysts tried are mainly the inorganic acids (boric, arsenic, uranic, phosphoric, molybdic, tungstic and titanic), hetero-acids (molybdophosphoric, tungsto-silicic etc.) and the acid salts of these acids[3]. These catalysts are generally used on carriers (carbon, graphite, coke and

silica gel) and various metals, chiefly those of Group VIII but copper, manganese, chromium, vanadium and some Group IV metals (titanium, thorium and zirconium) are also being used as promoters. Halides including fluorides and other fluorine compounds, particularly boron trifluoride and the oxides of various metals have also been used. For the reaction of the homologues of methanol with carbon monoxide in a flow system at 200 atm. pressure, 87% phosphoric acid containing copper phosphate has been used by Hardy[4]. Remarkable progress in this field of chemistry was achieved when the carbonyls of Group VIII metals were first used as catalysts.

In 1941 Reppe and co-workers[5] showed that in the synthesis of carboxylic acids from carbon monoxide and alcohols, metal carbonyl and halide mixture act as effective catalysts. Carbonyl-forming metals with added cuprous chloride or iodine can also be used as catalysts[6].

Bhattacharyya and co-workers[7] studied in detail the synthesis of carboxylic acids and esters from carbon monoxide and alcohols at 200°-300°C and 200-400 atm. with Ni, Co and Fe catalysts. A number of Ni and $NiI_2$ catalysts deposited on silica gel were tested and were found to be highly active. The catalytic activity followed the order

$$nickel > cobalt > iron,$$
$$iodide > bromide > chloride.$$

Under their optimum conditions (temp. 180°-230°C and pressure 280 atm.) in the synthesis of acetic/propionic acid from carbon monoxide, methanol/ethanol in presence of $NiI_2$ supported on silica gel ($NiI_2$ = 84.2%) Bhattacharyya and co-workers[8] obtained

46% conversion of methanol to acetic acid and 37.3% conversion of

ethanol to propionic acid; corresponding yields of methyl and

ethyl esters in both cases were very low. Natta and Pino[9]

obtained a 66.5% yield of acetic acid from carbon monoxide and

methanol at 230°-250°C and 400-600 atm. by using nickel carbonyl

as the catalyst. The same reaction has also been tried success-

fully in presence of a catalyst consisting of a silver halide or

its mixture with another metal halide[10] in the presence of water at

300°C and 100 atm. Koch and Haaf[11,12] synthesised carboxylic acids

by the reactions of alcohols (or alkenes) with formic acid at

atmospheric pressure in the presence of a large excess of concen-

trated sulphuric acid, which serves both to dehydrate the formic

acid and alcohols with the formation of carbon monoxide and alkenes

respectively and also to catalyse the addition of carbon monoxide

to the alkenes.

(iii) Reactions of carbon monoxide, olefins or olefinic

compounds and water or compounds containing active hydrogen atoms,

lead to the synthesis of saturated carboxylic acids and their

derivatives, lactones and alcohols. In such reactions nickel and

cobalt carbonyls or those salts of nickel and cobalt which are

converted into carbonyls during the reactions have been widely

used as catalysts.

Newitt and Momen[13], in presence of reduced nickel and phos-

phoric acid, under the pressure of 150-400 atmosphere and a

temperature of 250°-300°C, obtained 46.6% propionic acid from

carbon monoxide, ethylene, and water. They also found that instead

of water, when ethyl alcohol, benzyl alcohol, ammonia and aniline

were used they underwent similar reactions with carbon monoxide and ethylene.

By passing propylene, steam and carbon monoxide through phosphoric acid at 200°C and 200 atm. Hardy[14] obtained hydrocarbons as well as carboxylic acids.

Bhattacharyya and co-workers[15] have thoroughly investigated the synthesis of propionic acid from carbon monoxide, ethylene and water in presence of $CoI_2$ supported on silica gel ($Co:SiO_2 = 50:50$) and $NiI_2$ supported on silica gel ($Ni:SiO_2 = 50:50$) at 230°-300°C and 300 atm. The maximum yields of propionic acid after a residence period of 3 hours have been reported to be 7.3% and 27.9% respectively. 50-85% yield of propionic acid has also been obtained in the presence of cobalt propionate or butyrate in aqueous medium at 200°-225°C, 135-270 atm. and at a ratio of $C_2H_4$ : CO as 1:3.

Esters may predominate in the reaction products when the formation of carboxylic acids from alkenes and carbon monoxide takes place in presence of alcohols. Natta, Pino and co-workers[16,17] used the catalysts based on cobalt extensively in the synthesis of esters from carbon monoxide, alkenes and alcohols.

Reppe and co-workers[18] synthesised esters from alkenes, alcohols, and carbon monoxide in the presence of carbonyl forming metals. In the synthesis of methyl propionate from carbon monoxide, ethylene and methanol, Bhattacharyya and co-workers[19], obtained the yields of 26.0%, 20.0% and 27.1% by using $CoI_2$, $NiI_2$ and $FeI_2$ supported on silica gel ($M:SiO_2 = 50:50$, where M = Co, Ni, and Fe) respectively, at 300 atm. and 230°-300°C. When methyl alcohol

was replaced by ethyl alcohol, the yields of ethyl propionate were found to be 25.1%, 24.4% and 23.4% respectively.

The synthesis of carboxylic acids from alkenes, carbon monoxide and water at 130°-375°C and upto 700 atm. has been described in various patents and papers. By the reaction of aliphatic unsaturated monocarboxylic acids and their esters with carbon monoxide and water, dibasic carboxylic acids and their esters are obtained at 75°-300°C and 400-1000 atm. Mainly nickel and cobalt carbonyl, and nickel and cobalt salts, which may be converted into carbonyls during the reaction, are used as catalysts[20]. It has been reported that if the original alkene is replaced by an alcohol or alkyl chloride the same products may be obtained[21,22] in the presence of concentrated sulphuric acid.

(iv) Reactions of carbon monoxide, acetylene and water or other compounds containing active hydrogen atoms, generally known as carboxylation of acetylene, lead to the synthesis of acrylic acid and its derivatives. This process may also be employed for any substituted acetylene.

In 1939 Reppe[23,24] synthesised acrylic acid and its esters from acetylene, carbon monoxide and water or alcohols. Other compounds with active hydrogen atom were found to react in a similar way with acetylene and carbon monoxide. Thus, amines gave acrylic amides, mercaptans gave acrylic acid, thio esters or tautomeric thio acrylic esters.

Bhattacharyya and co-workers[25,26] investigated in detail the synthesis of acrylic acid and esters from carbon monoxide, acetylene and water/alcohols in the presence of iodides,

naphthenates and other salts of nickel, cobalt and iron. From their experimental findings they have concluded that nickel salts exhibited superior catalytic activity over others.

(v) Reactions of carbon monoxide with aliphatic aldehydes and water or alcohols leading to the formation of aliphatic hydroxy acids and its esters have been studied recently in detail by Bhattacharyya and co-workers[27,28,29]. They have published their findings on the synthesis of glycollic acid and lactic acid and their esters by utilising formaldehyde and acetaldehyde respectively. A patent by Loder[30] discloses a process which involves the reactions, in the presence of a solvent and in the liquid phase of carbon monoxide and a compound of the general formula $RCH_2$-CHO in which R represents H or an alkyl, aryl, cyclic or alicyclic radical, under super atmospheric pressure and at temperatures of $50°$-$350°C$.

The reaction of carbon monoxide with higher ketones has met with little success. Hardy[31] observed that when a mixture of acetone and water vapour was passed with carbon monoxide through liquid phosphoric acid at 200° to 210°C, a mixture of acetic and pivalic acids were formed in the molar ratio of 2 : 1.

(vi) Reactions of carbon monoxide with cyclic and aliphatic ethers leading to the formation of carboxylic acids and esters have been investigated by Bhattacharyya and co-workers[32a,32b]. They obtained maximum yield of adipic acid to the extent of 23.3% from tetrahydrofuran and 28.9% of ethyl propionate from diethyl ether using iron, cobalt and nickel iodide supported on silica gel. In presence of nickel ammonia complexes of phosphonium

halides Reppe[33] has also obtained quite good yields of esters from ether and carbon monoxide.

(vii) Primary and secondary amines react with carbon monoxide or a wide variety of metal carbonyls, forming the N-formyl derivatives and urea. Many of these reactions take place even at room temperature and pressure. The formation of formanilide from aniline and a small quantity of aniline hydrochloride was reported by Buckley and Ray[34], at 250°C and a carbon monoxide pressure of 3000 atm. The behaviour of tertiary amines on carbonylation is very interesting. Aliphatic tertiary amines on carbonylation are reported[35,36] to give N, N-dialkyl formamides. On the other hand aryl tertiary amines are reported to react as shown below where R is an alkyl group.
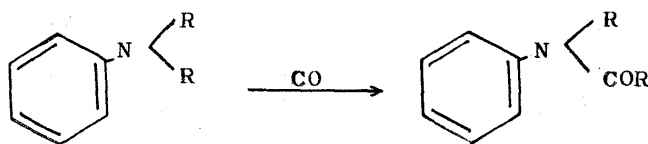


Sampson[37] reported that hydrazine hydrate reacts with iron pentacarbonyl at 45°C under a carbon monoxide pressure of 900 atm. to give semicarbazide, while at 100°C and 500 atmospheres both urea and semicarbazide are formed. Totally different products are obtained from hydrazine hydrate and carbon monoxide in the absence of a catalyst[38]. It has also been reported elsewhere[39] that semicarbazide and ammonia were obtained when hydrazine and carbon monoxide reacted at 20° to 50°C and 50 to 1000 atm.

(viii) Buckley and Ray[40] found that many organic compounds were reduced by carbon monoxide under anhydrous conditions at high temperature and pressure with the formation of carbon dioxide.

In the absence of catalysts at 150° to 250°C and at 3000 atmospheres nitro, nitroso, and azoxybenzenes were reduced to azobenzene $C_6H_5N = N \ C_6H_5$; N-phenyl hydroxylamine was reduced to aniline. In presence of Raney cobalt, benzyl alcohol, phenyl methyl carbinol and benzhydrol were reduced to the corresponding hydrocarbons. Some of the reactions cited above (vii) can also be classed under this category.

(ix) Reactions of organo metallic compounds, such as Grignard's reagent[41], metal alkyls and carbon monoxide have also been utilised to synthesise various aliphatic as well as aromatic compounds of industrial importance such as alcohols, acids, aldehydes, ketones and unsaturated hydrocarbons.

(x) Metal carbonyls or carbon monoxide have been used to synthesise carboxylic acids or esters from alkyl or aryl halides. The literature on this subject is, however extremely meagre, excepting a few patents. It has been disclosed in the patents that the treatment of an alkyl/aryl halide with nickel carbonyl, water and carbon monoxide at temperatures around 300°C and at a pressure of carbon monoxide of about 600 atm. to give around 30% yield of the corresponding alkyl/aryl carboxylic acid. The use of iron and cobalt carbonyl apart from nickel carbonyl in the above reaction has been disclosed by a patent by Bliss and Southworth[42]. In a recent publication Tripathy et al[43] have reported that 80% of benzoic acid can be produced from chlorobenzene, carbon monoxide and water in presence of nickel iodide supported on silica gel ($Ni:SiO_2 = 50:50$).
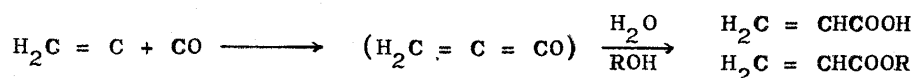
The use of a copper-zinc catalyst in the carbonylation of
aryl halides has been patented[44], but the uncertainty is whether
this involves a metal carbonyl intermediate. It has been repor-
ted that if in the carbonylation of aryl halides, anhydrous
alcohols[45,46] are used as the reaction medium instead of water,
the corresponding esters are obtained.

Yamamoto, K. and Kato, S.[47] claimed to have obtained
appreciable yield of phthalic acid together with some chloro-
benzoic acid from the carbonylation of o-dichlorobenzene under
pressure using nickel carbonyl and iodine as catalyst, but the
details are covered by patent. In another patent[48] Kröper, Wirth
and Huchler have claimed that aromatic carboxylic acids, their
esters and salts could be prepared by the reaction of halogenated
hydrocarbons with formates at elevated temperatures. According to
that work, when p-dichlorobenzene was heated with sodium formate in
a carbon monoxide atmosphere, the temperature, pressure and resi-
dence period being around 320°C, 110 atm. and 6 hours respectively,
terephthalic acid could be obtained. The reaction was catalysed
by finely divided Cu, Ag, Fe, Co or Ni in the metallic state or as
carbonyls or metal halides. Some German patents[49,50,51,52]
claimed that dicarboxylic acids or their esters could be produced
through the carbonylation of corresponding dihalobenzenes.
Romanovskii and Artemev[53] in a paper on carbonylation of p-dichloro-
benzene have also claimed to have obtained terephthalic acid.

Mechanism of carboxylation reactions :

The mechanism of carboxylation naturally depends to a
considerable extent on the catalyst used. In a discussion of the

mechanism of the carboxylation of acetylene in the presence of nickel carbonyl, Reppe[15] considers the possibility that the CO reacts with the iso-form of acetylene with the intermediate formation of methylene-keten which subsequently can react readily with water or alcohol to give acrylic acid or its esters :
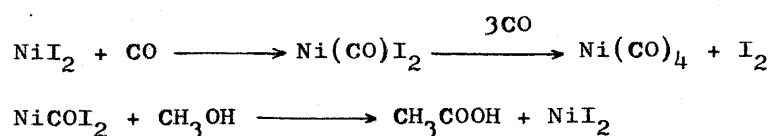
$$H_2C = C + CO \longrightarrow (H_2C = C = CO) \xrightarrow[ROH]{H_2O} \begin{array}{l} H_2C = CHCOOH \\ H_2C = CHCOOR \end{array}$$

The keten scheme cannot, however, explain either the reactivity of symmetrically disubstituted acetylenes or the formation of two reaction products.

A mechanism[54] according to which the reagent with labile hydrogen reacts with the metal carbonyl catalyst to give intermediate compounds was proposed. This intermediate in turn react with alkenes to form new intermediate compounds in which one carbon atom in the alkene is joined directly to the central atom of the metal carbonyl.

Natta et al.[55,56] suggested a new mechanism for the carboxylation of alkenes with carbon monoxide in the presence of a catalyst based on metallic cobalt. According to their scheme, the active catalyst is the intermediate cobalt carbonyl hydride $Co(CO)_3COH$. This adds on to the double bond of the alkene to form an intermediate compound which then reacts with the compound containing labile hydrogen.

The formation of cobalt carbonyl hydride does not require the presence of large quantities of hydrogen, and small quantities of water or hydrogen sulphide are sufficient[57].
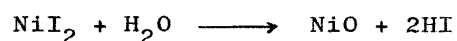
For carboxylation reactions in the presence of metallic nickel and nickel halides on carriers, Bhattacharyya[58] proposed two basic schemes with intermediate metal carbonyl halide complexes or carbonium ions. The first scheme gives complexes of the type $M(CO)I_2$ (where $M$ = Co, Fe, Ni), which subsequently react with other reagents; CO may be added on with the liberation of halogen, for example,

$$NiI_2 + CO \longrightarrow Ni(CO)I_2 \xrightarrow{\;3CO\;} Ni(CO)_4 + I_2$$

$$NiCOI_2 + CH_3OH \longrightarrow CH_3COOH + NiI_2$$

Here $NiI_2$ is regenerated.

In the reaction of Fe and Co halides under pressure, complexes of composition $Co(CO)I_2$, $Fe(CO)_2I_2$, $\left[Fe(CO)_3Br_2\right]$ 3 etc. are formed[57,59]. $Co(CO)I_2$ is obtained at 200 atm. and 100°C in the form of a dark red crystalline substance with a very high CO dissociation pressure even at room temperature. The analogous nickel complexes could not be isolated, although they may be formed as unstable intermediate products. The electronic configuration of Ni, Co, and Fe indicate that the stability of these complexes decreases in the order Fe $>$ Co $>$ Ni. On the one hand, the Ni complexes are the least stable and hence more reactive and on the other hand, iodide forms complexes more readily than bromide and chloride. The scheme involving intermediate carbonyl halide complexes cannot, however, explain the activating action of traces of water on the catalyst. The other scheme, based on the carbonium-ion theory, is therefore more probable, in view of the acidic character of the catalysts on silica gel.

It was mentioned above that the presence of traces of water is necessary to preserve the activity of the $MX_2$ catalysts. This is evidently required for the formation of HI according to the rection
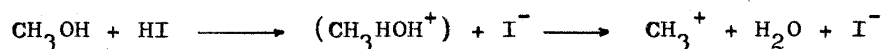
$$NiI_2 + H_2O \longrightarrow NiO + 2HI$$

or, according to Reppe,

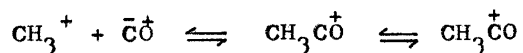$$NiI_2 + 5CO + H_2O \longrightarrow Ni(CO)_4 + 2HI + CO_2$$
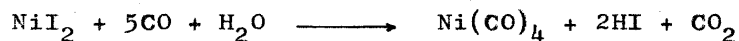
Traces of nickel oxide are in fact detected in the spent catalyst. The function of HI may be to displace the extremely active CO from the nickel carbonyl with regeneration of $NiI_2$ :
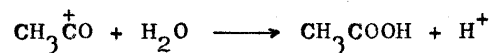
$$2HI + Ni(CO)_4 \longrightarrow NiI_2 + 4CO + H_2$$
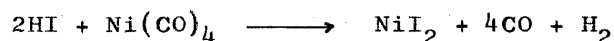
or to activate other components of the reaction,

$$CH_3OH + HI \longrightarrow (CH_3HOH^+) + I^- \longrightarrow CH_3^+ + H_2O + I^-$$

The resulting carbonium ion reacts with CO,

$$CH_3^+ + \bar{C}\overset{+}{O} \rightleftharpoons CH_3\overset{+}{CO} \rightleftharpoons CH_3\overset{+}{CO}$$

Water, then reacts with the formation of acetic acid,

$$CH_3\overset{+}{CO} + H_2O \longrightarrow CH_3COOH + H^+$$

The $H^+$ then attacks another alcohol molecule and the reaction continues. The mechanism of other reactions involving the formation of acids and esters may be represented in this way[60,61].