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Catalytic synthesis of organic compounds by the carbonylation of unsaturated hydrocarbons and alcohols

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ABSTRACT. The methods of synthesis of organic compounds by the carbonylation of acetylene, diene, and alkene hydrocarbons as well as alcohols in the presence of homogeneous and heterogeneous catalysts based on Group VIII metals and acid catalysts are examined. Data are presented on the synthesis of unsaturated and saturated mono- and di-carboxylic acids and their esters, lactones, and ketones from hydrocarbons and alcohols as well as the activities, selectivities, and stabilities of the catalytic systems in the carbonylation reaction.
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I. Introduction

During recent years, the world industrial output based on the use of carbon monoxide has expanded significantly. The synthesis of methanol and of liquid hydrocarbons from CO and H_2 (the synthesis gas), the hydroformylation of olefins, and the carbonylation of methanol with formation of acetic acid may be regarded as some of the processes carried out on a large scale.

The development of processes based on the use of carbon monoxide is associated with many factors. The principal of these is the necessity to employ new alternative sources of raw materials. Since the 1940s, petroleum has been the principal source of raw materials for the chemical industry, which led to the creation of an independent branch of industry—petrochemistry. However, in recent years a tendency has arisen towards a decrease in the rate of extraction of petroleum, the principal petroleum deposits tend to become exhausted, and there is a trend towards a shift of the main centres of petroleum extraction in the USSR to the regions of the North, the North West, and the Far West. These factors led to the increase in the cost of prospecting for and the extraction and transport of petroleum and hence has necessitated the search for new ways of replacing it. Since the USSR has enormous resources in coal, shale, and natural gas, the intensification of their chemical processing in order to obtain valuable organic compounds, which are nowadays produced on the basis of petroleum, is extremely promising.

In particular, carboxylic acids, hydroxyacids, acid anhydrides, lactones, alcohols, ethers and esters, and aldehydes and ketones can be obtained via carbonylation. Many of these reactions have been fairly thoroughly investigated but so far sufficiently active, selective, and stable catalytic systems, which would permit the introduction of promising processes into industry, have not been created in many instances.

The present review includes data on the latest advances in the catalytic syntheses of oxygen-containing compounds by the catalytic carbonylation of acetylene, dienes, olefins, and alcohols in the presence of homogeneous and heterogeneous catalysts based on Group VIII metals or acid catalysts.

II. Carbonylation of unsaturated hydrocarbons

A wide variety of carbonyl-containing products of practical value are obtained by the carbonylation of unsaturated compounds containing triple, double, or conjugated bonds. The interest in this reaction has grown particularly in recent years in connection with the necessity to create new technological methods for the synthesis of valuable chemical products on the basis of natural gas and coal from which mixtures of carbon monoxide and hydrogen can be readily obtained.

A series of monographs and reviews have been devoted to the carbonylation reactions of unsaturated compounds.[1-3] Below we shall therefore examine only the publications of recent years as well as problems of a general character.

The possibility of obtaining acetylene hydrocarbons from a non-petroleum raw material leads to good prospects for the application of processes involving the carbonylation of these substrates.

1. Carbonylation of acetylene hydrocarbons

The carbonylation of acetylene hydrocarbons usually leads to the formation of acrylic acid, its derivatives, and esters:[4-20]

$$R{-}C{\equiv}CH + CO{-}\begin{cases}\xrightarrow{H_2O} CH_2{=}C(R)COOH\\ \xrightarrow{R'OH} CH_2{=}C(R)\,COOR'.\end{cases}$$

For example, mixtures of maleic and fumaric acids have been obtained in 35–40% yield by the carbonylation of acetylene in the presence of H_2PdBr_6.[4] The reaction is carried out at atmospheric pressure and a temperature in the range 35–40 °C by passing a 4 : 1 mixture of CO and C_2H_2 through a hydrochloric acid solution. The maleic acid formed together with fumaric acid then isomerises fully to fumaric acid. When $PdBr_2$ mixed with oxidants [$FeCl_3.6H_2O$, $Fe_2(SO_4)_3.9H_2O$, O_2] is used as the catalyst, a mixture of fumaric and maleic acids and maleic anhydride is obtained from acetylene and its homologues.[5] The anhydride of phenylmaleic acid has been obtained from phenylacetylene under these conditions.

The carbonylation of acetylene and some of its homologues in the presence of palladium catalysts in the liquid phase containing HCl and HBr takes place with formation of acrylic acid and its esters and β-chloroacrylic acid and its esters. It has been studied in detail in a number of investigations.[6-12] *trans*-β-Chloroacrylic acid has been obtained in 62.5% yield from a 4:1 C_2H_2–CO mixture in HCl solution in the presence of $PdCl_2$–$HgCl_2$ with added NH_4Cl and $FeCl_3$ at 80.5 °C and atmospheric pressure.[6] Vinyl chloride and small amounts of acetaldehydes are formed as side products.

The carbonylation of acetylene also takes place in the presence of the $PdBr_2$–HBr–oxidant–BuOH system with added PPh_3. $FeCl_3$, O_2, and quinone are used as oxidants.[7,8] In order to increase its rate, the reaction is carried out in carboxylic acid amides.[8]

The rate of carbonylation of acetylene (70 °C, atmospheric pressure) is described by the following equation when the $PdBr_2$–$P(OPh)_3$–HBr.ROH catalytic system is used:[9]

$$r = k_1 p_{CO} p_{C_2H_2} / [H^+] \times (1 + k_2 p_{CO} p_{C_2H_2} + k_3 p_{C_2H_2}),$$

where k_1, k_2, and k_3 are constants and p_{CO} and $p_{C_2H_2}$ are the current partial pressures of carbon monoxide and acetylene respectively.

In the presence of the PdI_2–LiI–HCl–ROH catalyst, the kinetics of the carbonylation of acetylene are described by a more complex equation.

The "alkoxide" reaction mechanism has been proposed:[9]

$$PdX_2 \underset{HX}{\overset{ROH}{\rightleftharpoons}} XPdOR \xrightarrow{CO} XPdCOOR \xrightarrow{C_2H_2} XPdCH{=}CHCOOR - \begin{cases} \xrightarrow{H^+} CH_2{=}CHCOOR + PdX_2, \\ \xrightarrow{CO,ROH} (ROOCCH{=})_2 + HX + Pd(0). \end{cases}$$

The activity of complexes of the type $Pd\{P(OR)_3\}X_2$ in the carbonylation of acetylene in hydrochloric acid and 1-butanol diminishes in the sequences $Cl^- > Br^- > I^- > SCN^-$ and $P(OCH_3)_3 > P(OC_2H_5)_3 > P(O\text{-iso-}C_3H_7)_3$. When the reaction is carried out in hydrobromic acid, the opposite sequences are observed. The addition of LiI to the reaction medium appreciably increases the activity of the catalytic system. Palladium complexes with ligands in the *trans*-positions possess a higher activity. The main product of the carbonylation of acetylene is the monoester of acrylic acid. The formation of dicarboxylic acid diesters is hardly observed.[10,11]

Quinone is an effective oxidant when the PdI_2–LiI–HCl–BuOH catalytic system is used for the carbonylation of acetylene with formation of acrylic, propionic, maleic, fumaric, and succinic acid esters. The Pd^+ ion is then responsible for the catalysis. The activity of the complexes $MPdI_2.2H_2O$ (where M = Li or Cs) is significantly higher than that of the complexes $[Pd(CO)Cl]_n$ and $Cs[Pd(CO)Cl_2]$.[8]

The carbonylation of methylacetylene in the presence of a catalytic system containing $PdCl_2$ and HI in methanol and acetone at 50 °C and a pressure of 24 atm afforded methyl methacrylate and methyl crotonate in overall yields of 97.0 and 2.0% respectively.[12,14] The reaction takes place effectively not only in alcohol but also in other oxygen-containing compounds, for example, methyl and ethyl acetates, ethyl methyl ketone, tetrahydrofuran (THF), dioxan, and acetone.

The carbonylation of acetylene, methylacetylene, phenylacetylene, and other alkyl- or aryl-acetylenes can be achieved in the presence of a wide range of palladium complex catalysts containing various ligands.[15,16] Thus acetylene reacts readily with CO and O_2 in the presence of PdX_2, where X = Cl, Br, or I, at temperatures in the range 0–70 °C and atmospheric pressure with added thiourea.

Methyl maleate with a small admixture of fumaric acid ester as well as the diesters of *cis,cis*-, *cis,trans*-, and *trans,trans*-muconic acids are mainly formed in methanol and acetone at 15 °C from CO, C_2H_2, and O_2 in proportions of 1:1:0.1 in the presence of $PdCl_2$ and thiourea.[15]

Maleic and fumaric acid esters are obtained from acetylene, CO, and O_2 at 20 °C and atmospheric pressure in the presence of $PdCl_2$ and ethanol with the following aminoacids as additives: DL-threonine, L-glutamic acid, DL-lysine.HCl, *N*-methylglycine, L-α-alanine, DL-β-phenyl-α-alanine, and DL-serine.[16]

Nickel catalysts are also effective in the carbonylation of acetylene. Ethyl 3,4-diacetoxy-2-methylenebutyrate, whose hydrolysis affords the valuable antibacterial preparation methyl βγ-dihydroxy-α-methylenebutyrate, is formed from 1,2-diacetoxybut-3-yne in solution in an alcohol–acetic acid (or an alcohol–benzene) mixture in the presence of nickel carbonyl under mild conditions (70 °C, atmospheric pressure).[17]

Derivatives of alkylidenesuccinic acids have been synthesised from acetylene alcohols having the general formula RR'C(OH)C≡CH and carbon monoxide by carbonylation under pressure in the presence of palladium black and HI in benzene or in the presence of $CO_2(CO)_8$ with various additives.[18] The reaction proceeds in accordance with the mechanism

$$RR'C(OH)C{\equiv}CH + CO \rightarrow [RR'C{=}C{=}CHCOOH] \xrightarrow{CO,H_2O}$$
(I)
$$\rightarrow RR'C{=}C(COOH)CH_2COOH \rightarrow RR'C{=}\text{(III)}$$
(II)

The carbonylation of the alcohols (Ib) and (Ic) proceeds specifically. Thus a mixture of the aliphatic unsaturated methoxyacids (VI), (VII), and (VIII) as well as the lactone (IX) have been obtained from compound (Ib):

$(CH_3)_2C(OH)C{\equiv}CH$ (Ib) →
- $(CH_3)_2C{=}C(CO_2CH_3)CH_2CO_2CH_3$, (VI)
- $(CH_3)_2C(OCH_3)CH{=}CHCO_2CH_3$, (VII)
- $(CH_3)_2C(OCH_3)C(CO_2CH_3){=}CHCO_2CH_3$, (VIII)

(IX)

The carbonylation of the alcohol (Ic) results in the formation of a mixture of the methoxymonoester (X) and the diester (XI):

(Ic) $\xrightarrow{CO,CH_3OH}$ (X) + (XI)

Acetylene alcohols having the formula (I), where R = R' = H (Ia), R = R' = CH_3 (Ib), R + R' = $(-CH_2)_4$ (Ic), or R = CH_3 and R' = C_6H_5 (Id) have been converted into the anhydrides of the corresponding dicarboxylic acids (II) (Table 1) on interaction with CO under a pressure of 100 atm in benzene in the presence of palladium black and HI.

On refluxing with water, the anhydrides (IIIb–d) are converted into the corresponding acids (IIb–d).

The carbonylation of compound (Ia) in methanol leads to the formation of dimethyl itaconate (IV) and dimethyl aconitate (V) in proportions of 6:1 in an overall yield of 35%. The reaction

proceeds in accordance with the mechanism

$$HC{\equiv}CCH_2OH \xrightarrow[-H_2O]{CO,CH_3OH} [CH_2{=}C{=}CHCO_2CH_3] \xrightarrow{CO,CH_3OH} CH_2{=}C(CO_2CH_3)CH_2CO_2CH_3 \quad (IV)$$

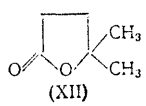
$$HC{\equiv}CCH_2OH \xrightarrow{CO,CH_3OH} CH_3O_2CCH{=}C(CO_2CH_3)CH_2OCH_3 \xrightarrow{CO} CH_3CO_2CH{=}C(CO_2CH_3)CH_2CO_2CH_3 \quad (V)$$

Table 1. Carbonylation of acetylene alcohols in benzene in the presence of palladium black and HI.[18]

Acetylene alcohol	T, °C	p_{CO}, atm	t, h	Reaction product	Yield of reaction product, %
(Ia)	30	20	1.5	tar	—
(Ib)	50	20	3.0	(IIIb)	45
(Ic)	70	50	5.0	(IIIc)	36
(Id)	30	50	2.0	(IIId)	51

The carbonylation of the alcohol (Ib) in the presence of $Co_2(CO)_8$ with various additives (see Table 2) affords tetraconic anhydride (IIb) and the diester (VII). 5,5-Dimethyl-$\Delta^{3,4}$-dihydrofuran-2-one (XII) was also obtained in small amounts:[18]

$$(CH_3)_2C(OH)C{\equiv}CH \xrightarrow{CO,H_2O} (CH_3)_2C(OH)CH{=}CHCOOH \rightarrow$$



(XII)

Table 2. Carbonylation of ethynyldimethylmethanol (Ib) in the presence of cobalt catalysts (150 °C, 100 atm CO).[18]

Catalytic system	Overall yield of compounds (IIb), (VII), and (XII), %	Relative yields, %		
		(IIb)	(VII)	(XII)
$Co_2(CO)_8+HI+CH_3OH$	53.4	42.1	50.4	7.5
$Co_2(CO)_8+HI+Py+CH_3OH$	49.2	25.6	32.3	42.1
$Co_2(CO)_8+C_6H_6$	15.3	—	—	100.0
80.7% CoNaY (SiO_2/Al_2O_3=4.4)	58.3	28.8	47.9	23.3

Butyl acrylate and propionate, the diesters of maleic and fumaric acids, and also crotonic acid esters can be obtained by carbonylating acetylene in the presence of $Pd(NH_3)_nX_2$ (where n = 2 or 4 and X = Cl or I) and HCl at 70 °C and atmospheric pressure in the liquid phase.[19,20] A 1 : 1 mixture of CO and C_2H_2 is used in the reaction. Palladium is regenerated by treating the reaction solution with a stream of dry NH_3 and subsequently isolating the palladium complex by filtration. Under the conditions indicated, the overall rate of formation of the carbonylation products is 1.45 mol litre^{-1} h^{-1}.[19]

Thus a wide variety of mono-, di-, and tri-carboxylic acids, their esters and anhydrides, lactones, and cyclic compounds can be obtained by carbonylating acetylene compounds and their homologues. However, the industrial application of these processes is prevented in the first place by the insufficient activity and selectivity of the proposed catalytic systems.

We may also note that complexes based on Group VIII noble metals are very costly, while nickel complexes are extremely toxic and volatile. In addition, the use of homogeneous complex systems requires the creation of complex regeneration schemes.

2. Carbonylation of dienes

When dienes interact with carbon monoxide in aqueous or alcoholic media, unsaturated monocarboxylic acids, saturated dicarboxylic acids, or their esters, lactones, and mono- and polyketones are formed.[1-3,21] Butadiene and its oligomers, allene, keten, the di- and tri-oligomers of cyclopentadiene are most often used as substrates in this reaction.

The carbonylation of the simplest diene (buta-1,3-diene) in methyl or ethyl formate takes place under mild conditions (120 °C, 30 atm) mainly with formation of the pent-3-enoic acid ester.[22] Pent-3-enoic acid itself is formed in small amounts. Cobalt carbonyl with added isoquinoline is used as the catalyst. The process selectivity increases after the introduction of amines with pK_a = 3–11 into the reaction zone as cocatalysts and also on raising the reaction temperature to 140 °C and the CO pressure to ~900 atm.[23] The presence of admixtures of acetylene hydrocarbons in buta-1,3-diene lowers the efficiency of the process. In the presence of $Co_2(CO)_8$ and pyridine, methyl pent-3-enoate can be obtained in 78% yield from buta-1,3-diene containing about 5% of vinylacetylene, CO, and methanol at 135 °C and a pressure of 900 atm. A decrease in the vinylacetylene content to 0.1% increases the yield of the product to 98%.

In the presence of the $Pd(OAc)_2-Ph_2P(CH_2)_2.PPh_2$ catalytic system (110 °C, 50 atm), a mixture of the isopropyl esters of pent-3-enoic and nona-3,8-dienoic acids is formed from buta-1,3-diene, CO, and isopropyl alcohol in 26.0 and 13.5% yields respectively.[24] The use of C_1–C_{12} aliphatic alcohols makes it possible to regenerate the palladium to the extent of 90%.

The selectivity of the carbonylation of buta-1,3-diene with formation of pen-3-enoate esters increases after the introduction of a mixture of pyridine and isoquinoline into the reaction zone together with $Co_2(CO)_8$. Under these conditions, mainly only the target product is formed from the butadiene at 100–140 °C. Side compounds—4-vinylcyclohexene, dibutyl ketone, methyl α-methylglutarate, and butenals—are formed in insignificant amounts.[25]

A method has been proposed for the synthesis of the phenyl esters of pent-3-enoic and pent-2-enoic acids by carbonylating buta-1,3-diene with carbon monoxide in the presence of compounds having the formula $HX.C_6RR^1R^2R^3R^4$, where X = O or S and R – R^4 = H, alkyl, alkoxy-group ($\leqslant C_6$), cycloalkyl, cycloalkoxy-group (C_3–C_{12}), aryl, and aryloxy-group (C_6–C_{12}), in the presence of $Co_2(CO)_8$ and nitrogen-containing bases with pK_a = 3–10, namely pyridine, γ-picoline, isoquinoline, or their mixtures.[26] The carbonylation of the butadiene is accompanied by dimerisation, which results in the formation of a nona-3,8-dienoate ester:

$$2CH_2{=}CHCH{=}CH_2 + CO + ROH \rightarrow CH_2{=}CH(CH_2)_3CH{=}CHCH_2COOR .$$

It has been suggested that the coupled dimerisation and carbonylation reactions be carried out in the presence of palladium salts or complexes together with sodium, lithium, and potassium acetates.

The catalytic systems are stabilised by arsines, stibines, or phosphines in aliphatic, cyclic or aromatic alcohols and heterocyclic compounds containing oxygen, sulphur, and nitrogen atoms: THF, tetrahydropyran, dioxan, lactones, diketones, tetrahydrothiophen, dibenzothiophen, benzo-1,3-dioxole, etc. Thus isopropyl nona-3,8-dienoate was formed in 85% yield from butadiene, CO, and isopropyl alcohol in the presence of $Pd(OAc)_2$ and PPh_3 at 110 °C and a CO pressure of 50 atm after 18 h.[27]

Allene is carbonylated in the presence of $(Et_2NH)_2NiI_2$ and Et_2NH under mild conditions (20 °C, 5–10 atm CO).[28] For the $(Et_2NH)_2\ NiI_2 : CH_2=C=CH_2 = 1:2$ ratio, a mixture of $Et_2NC(O).C(=CH_2)CH_2NEt_2$ and $Et_2NC(O)C(=CH_2)CH_2C(=CH_2)CH_2NEt_2$ is formed in 48 and 12% yields in solution in a THF–ether mixture. For the equimolar reactant ratio, the yields of these products are 57 and 0.9% respectively. They are formed from allene, Et_2NH, and CO via the intermediate $Et_2NC(O).(=CH_2)CH_2NiI(Et_2NH)_n$.[28] Alkyl esters of malonic acid, which are used in the industrial synthesis of malonic and barbituric acids and medicinal drugs, are obtained by the interaction of keten $CH_2=C=O$ with CO in nitrous acid esters RONO in the presence of phosphine-containing complexes L_2MX_2 (where M = Pt, Pd, Rh, Ru, or Ir and X = Cl, Br, or I), tin halides, and quaternary ammonium salts $R'_4N.X$.[29]

A process has been developed for the syntheis of formylvaleric acid by carbonylating buta-1,3-diene with subsequent hydroformylation of the pent-3-enoic acid ester formed in accordance with the scheme[30]

$$CH_2=CHCH=CH_2 + CO + ROH \rightarrow CH_2=CHCH_2CH_2COOR \rightarrow \xrightarrow{CO,\ H_2} HCOCH_2CH_2CH_2CH_2COOR\ .$$

The first stage is carried out at 135 °C and a CO pressure of 900 atm and the second stage is performed at 120 °C and a pressure of 200 atm. The methyl formylvalerate formed is used in the manufacture of plasticising agents, ε-caprolactam, ε-caprolactone, hexanediol, and adipic acid.

The selective carbonylation of dienes, in particular buta-1,3-diene,[31] can be achieved in a two-phase system consisting of a layer of a polar liquid (water, MeCN, DMF, DMSO, $MeNO_2$, *N*-methylpyrrolidinone, and C_1-C_4 alcohols) and a layer of a non-polar liquid with a dielectric constant $\varepsilon < 2.3$ (pentane, isopentane, hexane, iso-octane, cyclo-octane, tetradecane, etc.). The non-polar solvents then contain the reaction products and the layer of polar liquids contains the components of the catalytic system which are returned to the process. The catalysts are palladium and its compounds. Palladium catalysts on carriers promoted by nitrogen, phosphorus, and arsenic compounds and quaternary ammonium compounds, containing substances capable of generating hydrogen halides in the course of the reaction. Thus, ethyl esters of pentenoic acid (in 61.0% yield) as well as a mixture of diethyl α-methylglutarate and ethyl nona-3,8-dienoate are formed from buta-1,3-diene, CO, and ethanol in the presence of $(C_3H_4)_2PdCl_2$, Bu_4NCl, and 1-chlorobut-2-ene (source of HCl) at 120 °C and a pressure of 196 atm. After the treatment of the products with a mixture of hexane and methanol, the components of the catalytic system are extracted from the methanol phase and the reaction products are extracted from the hexane phase.

The esters of nona-3,8-dienoic acid are obtained selectively from butadiene in the presence of palladium complexes with phosphines and of a thiol as a stabiliser.[32] Thus methyl nona-3,8-dienoate has been obtained in 75% yield from buta-1,3-diene, CO, and methanol in the presence of the complex $Pd(OAc)_2.[P(iso\text{-}Pr)_3]_2$ with added $P(iso\text{-}Pr)_3$ and BuSh (stabiliser) at 100 °C and a pressure of 52.5 atm. Palladium black is not formed during the reaction, which indicates the stability of the catalytic complex.

Esters of but-2-ene-1,2-dicarboxylic acid have been obtained from butadiene under oxidative carbonylation conditions. The reaction is carried out in the presence of O_2, alkoxycycloalkenes, and alcohols. For example, treatment of butadiene with a mixture of carbon monoxide (7 atm) and O_2 (7 atm) in methanol and 1-methoxycyclohexene in the presence of $PdCl_2$, $CuCl_2$, and LiCl at 100 °C and a pressure of 126 atm gave rise after 2 h to dimethyl hex-3-enedioate in 84% yield for a diene conversion of 43%.[33,34]

Pent-3-enoic acid esters were obtained from butadiene, CO, and O_2 in the presence of $PdCl_2-CuCl_2$ as well as the additives PrCOONa and $HC(OMe)_3$. Thus *trans*-$(PhCH_2OOCCH_2CH=)_2$ is formed in ~80% yield in $PhCH_2OH$ at a CO pressure of 144 atm and a temperature of 60 °C.[35]

Pent-3-enoic acid diesters are obtained also without access of water and air in the presence of $PdCl_2$, $CuCl_2$, and alkali earth metal salts. The interaction of butadiene with CO in solution in anhydrous $CuCl_2$ in $PhCH_2OH$, NaOOCPr, and $HC(OMe)_3$ in the presence of $PdCl_2$ at 60 °C and a pressure of 3 atm resulted in the formation of the diester *trans*-$PhOOCCH_2CH=CHCH_2COOPh$.[36] This diester is hydrolysed to the unsaturated acid, which is then hydrogenated to adipic acid over a palladium catalyst.[36]

The selectivity of the conversion of butadiene into adipic acid diesters increases when mixtures of two bases of the pyridine and quinoline series, substituted by C_1-C_6 alkyls or alkenyls or by C_7-C_{10} alkylaryls or arylalkyls, are used as cocatalysts with $Co_2(CO)_8$. In the presence of the $Co_2(CO)_8$–pyridine–isoquinoline system butadiene interacts with CO and MeOH to form dimethyl adipate with a selectivity of 72.5% for a 100% conversion of the diene. When the $Co_2(CO)_8$–pyridine–γ-picoline catalytic system is used, the selectivity of the reaction with respect to the target product is 77.5%.[37]

A convenient technology has been proposed for the synthesis of adipic acid diesters via a two-stage scheme, where the first stage involves the preparation of the pent-3-enoic acid ester with utilisation of all the reaction side products and the regeneration of cobalt.[38–41] The catalyst is the $Co_2(CO)_8$, $HCo(CO)_4$ + pyridine (*N*-methylpyridine or *N*-methyldihydropyridine) system.

The synthesis of dimethyl butane-1,4-dicarboxylate from butadiene was improved by introducing the step involving the cooling to −5 °C of the products obtained in the first stage in the alcoholic phase (MeOH). This results in the formation of two phases: the reaction product (methyl pent-4-enoate) collects in the upper phase, while the lower, aqueous alcoholic phase contains up to about 98% of the cobalt catalyst, which is used in the second carbonylation stage.[41]

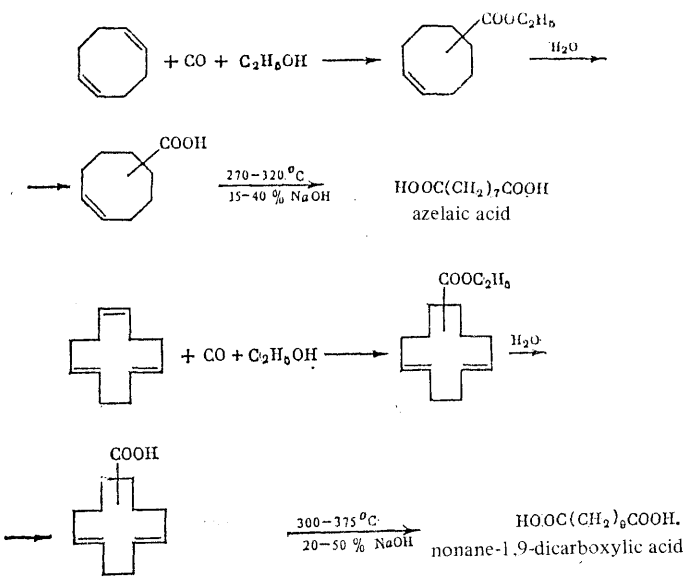
It has been shown[42] that the efficiency of the $Pd(OAc)_2-X_2$ (where X = phosphine) catalytic system in solution in amines [quinoline, lutidine, *NN*-diethylaniline, and 3,5-lutidine ($pK_a < 7$)] in the carbonylation of butadiene by carbon monoxide in an alcoholic phase (110 °C, 48 atm CO) with formation of the nona-3,8-dienoic acid ester increases with increasing basicity of the phosphines in the sequence $P(OPh)_3 < P(p\text{-}ClPh)_3 < PPh_3 < P(p\text{-}MePh)_3 < P(p\text{-}Bu)_3$. In the presence of tertiary amines with $pK_a > 7$ (*N*-methylmorpholine, *NN'*-dimethylpyridine, *NN'*-dimethylpiperazine, *N*-methylimidazole, etc.), the yield of the target products falls from 60–70 to 6–7%. The activity of the $Pd(OAc)_2$ $(PPh_3)_2$ catalytic system in amines with $pK_a < 7$ hardly changes after 32 cycles of its use, while the selectivity diminishes by 20%.

The structure and basicity of the ligands influence strongly the carbonylation of butadiene. For "strong" ligands ($pK_a < 6$), a ligand/Pd = 1–3 ratio is desirable, while for "weak" ligands ($pK_a < 6$) the ratio should be 4–100. Methyl nona-3,8-dienoate can be obtained in 60% yield from butadiene, CO, and methanol in the presence of $Pd(OAc)_2$, n-Bu_3P, and $(CNCC_2H_4)_3P$ at 90 °C and a CO pressure of 35 atm in the first stage for 2 h and at 110 °C in the second stage for 4 h.[43]

A continuous method has been developed for the synthesis of dialkyl adipates from butadiene, CO, and alcohols in the presence of the $Co_2(CO)_8$–pyridine–isoquinoline catalytic system with added hexane.[44] The first stage is carried out at 130 °C and a CO pressure of 300 atm, while the second stage is performed at 185 °C and 300 atm. The selectivity with respect to dimethyl adipate reaches 72.5%. In the absence of hexane, the selectivity is 66.4%.

Studies on the carbonylation of cyclic dienes (cyclo-octa-1,5-diene and cyclo-dodeca-1,5,9-triene), obtained from butadiene in the presence of nickel catalysts, are of great theoretical and practical interest.

A method has been proposed[45,46] for the preparation of azelaic acid from cyclo-octa-1,5-diene and of nonane-1,9-dicarboxylic acid from cyclododeca-1,5,9-triene by carbonylating dienes with formation of the corresponding unsaturated monocarboxylic acid esters and subsequent ring opening by refluxing in aqueous NaOH solutions.

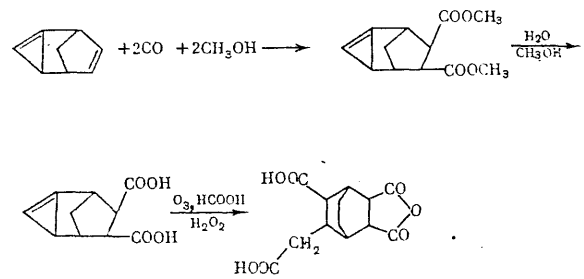


Cyclo-octa-1,5-diene is carbonylated in the presence of Rh(OAc).$(CO)(PPh_3)_2$ or Rh_2O using a 2 : 1–2 mixture of CO and H_2 at 70–85 °C and a pressure of 55–80 atm,[45] while cyclododeca-1,5,9-triene is carbonylated at 50–60 °C and a pressure of 250 to 300 atm.[46]

Ethyl cyclo-oct-4-ene-1-carboxylate has been obtained in yields up to 85–90% by carbonylating cyclo-octa-1,5-diene in the presence of $PdCl_2(PPh_3)_2$ and $AlCl_3$ in ethanol at 105–108 °C and a pressure of 100 atm.[47]

Cyclic di-, tri-, and tetra-carboxylic acids or their anhydrides, which are widely used in the industrial manufacture of plasticising agents, hardening agents for epoxy-resins, water-soluble polyester resins, and inks and dyes for printing and coatings, were obtained by carbonylating di- and tri-cyclopentadienes.[48–51]

The esters of dicyclopentadienedicarboxylic acids are obtained in high yields from dicyclopentadiene, CO, and alcohol in the presence of $Co_2(CO)_8$ and a pyridine base (pyridine, picoline, etc.). The process is carried out at a CO pressure of 20–40 atm in two stages: the first takes place at 100–120 °C and the second at 140–160 °C.[48] Dimethyldicyclopentenedicarboxylate is obtained by carboxylating dicyclopentadiene in the presence of $PdCl_2$, $CuCl_2$, and CH_3OH. It is then hydrolysed to the free acid, ozonised in formic acid, and oxidised to a tetracarboxylic acid and then further to the anhydride in accordance with the scheme[49]



The so called "tarry" carboxylic acids are obtained by carbonylating cyclopentadiene trimers and tetramers.[50] As in the carbonylation of dicyclopentadiene, which has the norbornadiene structure, in the presence of the $Co_2(CO)_8$ + pyridine catalytic system (50 atm CO, 80–140 °C) in methanol, methyl tricyclodecenecarboxylate and dimethyltricyclodecanedicarboxylate in porportions of 90 : 8 are obtained in an overall yield of ~80%.

The alkoxycarbonylation of butadiene is performed in isopropyl alcohol in the presence of $PdCl_2$ with added quaternary nitrogen-, phosphorus-, and arsenic-containing salts.[51] Extraction by saturated hydrocarbons to which the same quaternary salts have been added makes it possible to separate selectively methyl pent-3-enoate from the palladium catalyst present in the alcoholic layer. This ensures the stability of the catalytic system employed. The process takes place with a selectivity of 93.2%. The efficiency of the carbonylation of the cyclopentadiene trimer increases if some of the cyclopentadiene trimers or tetramers are hydrogenated in a preliminary step. The carbonylation of the partly hydrogenated cyclopentadiene trimer in the presence of NiI_2–H_2O (220 °C, 80 atm) yielded "tarry" carboxylic acids with a softening temperature of 42 °C.

In the carbonylation of buta-1,3-diene in the presence of $PdCl_2$ with addition of quaternary nitrogen-, phosphorus-, and arsenic-containing salts, 99% of the palladium passes to the isopropyl phase after the introduction into the reaction mixture of n-octane and Bu_4NCl. The specific activity of the catalytic system increases somewhat when it is reused. Analogous results have been obtained also in the carbonylation of butadiene in the presence of bis(π-allylpalladium dichloride) with the addition of the same salts and hydrogen halides.[52,53]

It has been suggested[54–56] that the products of the alkoxycarbonylation of dienes (including butadiene) in the presence of the $Co_2(CO)_8$–isoquinoline system be separated by distillation with subsequent refluxing of the separated product in benzene. The benzene layer is next treated with sulphuric acid and then with a Na_2CO_3 solution. The degree of extraction of cobalt is 99%.[52] Cobalt may be isolated from the reaction products also by treatment with air.[53]

3. Carbonylation of olefins

The interaction of olefins with CO and H_2O leads to the formation of unsaturated carboxylic acids having linear or branched structures. When water is replaced by alcohol, carboxylic acid esters are obtained. The structure of the acids formed depends primarily on the nature of the catalyst used and also on the conditions under which they are employed. In the presence of catalysts based on Group VIII metals, mainly mixtures of linear and branched α-methyl-substituted carboxylic acids are formed. When acid catalysts are used, the products are mainly branched αα-dialkyl-substituted carboxylic acids.

(a) Carbonylation of olefins in the presence of Group VIII metals and their complexes. When ethylene is carbonylated in the presence of metal complexes, propionic acid is formed.[58] The advantages of this method are its single-stage nature, high selectivity, and relative mild process conditions. Propionic acid is an important product used for the preparation of artificial fibres, the conservation of agricultural feed, and the manufacture of medicinal drugs and perfumes.

The synthesis of propionic acid by the carbonylation of ethylene has been achieved with a yield of 95% on the $Ni(OCOC_2H_5)_2$ catalyst at 285 °C and a pressure of 235 atm.[57] Nickel in the form of the carbonyl is extracted from the reaction mixture by treating it at 70–80 °C with an inert gas containing 3–10% of O_2. The acid obtained is used in the bread-baking industry.[58]

Effective catalysts based on mixtures of nickel and molybdenum or nickel and tungsten compounds have been proposed for the synthesis of propionic acid from C_2H_4, CO, and H_2O.[59] The reaction is carried out in the presence of iodine-containing promoting agents as well as amines or phosphines. Propionic acid has been obtained in 48.9% yield from ethylene (28 atm) and CO (28 atm) with added H_2 (3.5 atm) in the presence of $NiI_2.6H_2O$, $Mo(CO)_6$, and EtI at 175 °C in aqueous propionic acid. In the presence of NiI_2, $Mo(CO)_6$, and PPh_3, propionic acid is also formed in 56% yield from C_2H_4, CO, and H_2O.[60]

Together with heterogeneous palladium catalysts, homogeneous palladium systems are also effective in the carbonylation of C_2–C_4 olefins.[61–66] The $Pd(OAc)_2$, $Pd(OAc)_2(PPh_3)_2$, and Pd[poly-(2-vinylpyridine)]$_2Cl_2$ catalytic systems are active and selective in the carbonylation of ethylene (170 °C, 100 atm, C_2H_4/CO = 1). Propionic acid is formed in 65–70% yield.[61]

The reaction is carried out in acetic or propionic acid with the addition of Group I–III, VI, and VIII metals salts to the $Rh-Ru_3(CO)_{12}$ cluster and complexes based on it. The maximum yield of methyl esters of butyric acid is observed in the hexane–methanol–water mixture at 180 °C, an initial pressure of 28 atm, and a water concentration of 46.2 vol. %. The addition of $MoCl_6$ to the catalyst induces an increase in the activity of the system. It has been shown by UV spectroscopy that the change in activity is apparently associated with the formation of the $[Ru_3(CO)_{12-n}]Cl^{n-}$ anion stabilised by a M^{n+} metal ion.[62]

The carbonylation of olefins can occur in the presence of palladium catalysts obtained by the impregnation of zeolites or by ion exchange involving them.[61,63,64] High-silica zeolites, containing 0.5–1.0% of palladium, exhibit a high activity and selectivity in this reaction. Propionic acid has been obtained with a selectivity of 75–95% by carbonylating ethylene in aqueous acetic or propionic acid (140–190 °C, 20–80 atm). Partial hydration of ethylene results in the formation, together with propionic acid, of ethanol, from which ethyl acetate, ethyl propionate, and diethyl ketone are obtained with participation of ethylene. The optimum ethylene carbonylation conditions are created at a temperature of 170 °C and a pressure of 60 atm. Preliminary treatment of the Pd/NaM catalyst with air (350 °C, 5 h) and hydrogen (300 °C, 5 h) in succession increases the selectivity in the formation of propionic acid. The introduction of platinum instead of palladium into the zeolite increases sharply the degree of hydration of ethylene. Palladium-zeolite catalysts with a modulus $SiO_2/Al_2O_3 \geqslant 10$ are stable under the carbonylation conditions. In the presence of 1.2 wt. % of Pd/HSZ-1† (modulus = 47), propionic, butyric, and valeric acids have been obtained from CO and H_2O as well as C_2H_4, C_3H_6, and C_4H_8 respectively (170 °C, initial pressure 60 atm, 3 h). The degree of conversion then reached 98% and the overall selectivity in the formation of these three acids was 90–98%.[64]

The synthesis of cycloalkanecarboxylic acids from cyclo-olefins, CO, and H_2O is also of practical importance. These acids are used to synthesise medicinal drugs and preparations. Homogeneous palladium catalysts are active in the carbonylation of cyclopentene, cyclohexene, a 60 : 14 : 13 : 13 mixture of 1-methyl-, 3-methyl-, and 4-methyl-cyclopentenes and cyclohexene, as well as 1-methylcyclo-hexene, 4-methyl-cyclohexene, and 1-ethylcyclohexene with formation of the corresponding carboxylic acids.[65] The efficiency of the catalyst decreases in the sequence $Pd_3(CO)_3(PPh_3) > Pd(PPh_3)_2.(OAc)_2 > Pd(PPh_3)_2Cl_2 > Pd(OAc)_2 > PdCl_2$.

The carbonylation of cyclo-olefins in the presence of $Pd(PPh_3)_2Cl_2$ takes place most effectively in acetic acid. Mainly 2-methyl- and 3-methylcyclopentanecarboxylic acids are formed from a mixture of 1-, 3-, and 4-methylcyclopentenes. The formation of 1-methyl-cyclopentane-1-carboxylic acid is prevented by steric hindrance. A temperature of 150 °C and a CO pressure of 50–100 atm are optimal for the carbonylation of cyclo-olefins. Under these conditions, the yield of cyclic carboxylic acid is 80–90%.[65]

Acetals have been synthesised in high yields from olefins, CO, and H_2 in an alcoholic medium in the presence of cobalt carbonyl and added quaternary ammonium compounds. Thus the dimethyl acetal of tridecanal has been obtained with 90% selectivity and 10% conversion from dodec-1-ene and 1 : 1 mixture of CO and H_2 under pressure at 110 °C in methanol containing $Co_2(CO)_8$ and $PhCH_2M^+Me_3MeO^-$.[66]

The esters of branched carboxylic acids have been synthesised by carbonylating β-alkyl-α-olefins:[67] 2-ethylpent-1-ene, hex-1-ene, hept-1-ene, 2-butyloct-1-ene, 2-hexyldec-1-ene, 2-octyldec-1-ene, 2-hexyl-decyleicos-1-ene, or 3-propylhex-1-ene. The reactions were carried out at 180–200 °C and a pressure of CO with added H_2 of 50 to 250 atm in the presence of cobalt catalysts as well as nickel-containing compounds and pyridine bases as promoting agents. In the carbonylation of 2-ethyl-hex-1-ene in the presence of cobalt laurate and γ-picoline (185 °C, 180 atm) by carbon monoxide with added H_2 (3.5 atm) in methanol, the degree of conversion of the olefin was 90% and the selectivity with respect to methyl esters of nonanoic acids was 38%. The contents of the methyl esters of various acids in the mixture were 49.5% of the 4-methyloctanoate, 17% of the 6-methyloctanoate, and 18.5% of the 3-ethylheptanoate. The branched carboxylic acids obtained are widely used in the

†HSZ = high-silica zeolite.

synthesis of alcohols, amines, surfactants, emulsifying agents, plasticising agents, and components of synthesit lubricants.

A mixture of carboxylic acid esters has been obtained under analogous conditions from olefins, CO, and alcohols in the presence of the cobalt carbonyl–pyridine (alkylpyridine) catalytic system.[68] Their hydrogenation in the presence of a copper–chromium catalyst (250–350 atm, 180–220 °C) leads to the formation of alcohols which are intermediates in the synthesis of surfactants. Thus the carbonylation of a mixture of n-undecene, n-dodecene, and n-tridecene in methanol in the presence of cobalt carbonyl and γ-picoline yields a mixture of the methyl esters of C_{12}–C_{14} acids, which are hydrogenated to the corresponding C_{12}–C_{14} alcohols.[68]

The esters of linear saturated carboxylic acids are synthesised by carbonylating α-olefins and the esters of unsaturated carboxylic acids or the acids themselves are synthesised from dienes and acetylenes in the presence of palladium complexes $(R_3P)_2PdXR'$ (where R = alkyl, hydroxyalkyl, cycloalkyl, dialkylamine, thioalkyl, thioaryl, substituted or unsubstituted aryls, and piperidine or pyrrolidine groups and R′ = H, Cl, Br, C_1–C_5 alkyl, C_2–C_4 acyl, or arylalkyls up to C_{12}) and promoting agents—Ti, Tl, Ni, Fe, Cu, Mn, Cr, Pd, Zn, Co, or Sn chlorides. The interaction of hex-1-ene with CO (700 atm, 90 °C) in the presence of $PdCl_2(PPh_3)_2$ and $SnCl_2.2H_2O$ in ethanol results in the formation of C_7 acid esters consisting of 77% of the linear isomer.[69,70] The degree of conversion of hex-1-ene reaches 86%. C_7 acids, including 90% of oenanthic acid, are obtained in aqueous acetone (90 °C, 100 atm) from hex-1-ene in the presence of the $(PPh_3)_2PdCl_2.NH_2(CH_2)_2NH_2$ complex systems.[69,70]

Esters of linear carboxylic acids have been synthesised with a high selectivity under mild conditions in the presence of palladium complexes containing sterically hindered ligands.[71] Thus the esters of isopropanethiol with linear and α-methyl-substituted branched C_7 acids have been obtained in 78.8 and 7.1% yields respectively from hex-1-ene, CO, and alcohol in the presence of $Pd(OAc)_2$ and $(iso\text{-}Pr)_3P$ in solution in the $THF-(CH_3)_3CSH$ mixture (100 °C, 50 atm).

The isomeric composition of the esters formed in the methoxycarbonylation of hex-1-ene in the presence of $Co_2(CO)_8$ depends greatly on the nature of the medium, which also influences the rates of isomerisation and carbonylation of the olefin. For a methanol : hex-1-ene molar ratio of 10, the rates of isomerisation and carbonylation of hex-1-ene in pyridine are comparable (175–190 °C, 200–300 atm). In toluene, the rate of isomerisation of olefin is higher than the rate of its carbonylation, as a result of which esters of branched acids predominate in the products of the synthesis. The selectivity in the formation of the oenanthic acid ester increases with decrease in temperature and with increase in the CO pressure.[72]

Carboxylic acid esters are obtained[73,74] from α-olefins up to C_{12}–C_{13} in the presence of catalytic systems based on cobalt: $HCo(CO)_4$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, or $Co(CO)_3A_3$, where A = Bu_3P, $(C_{10}H_{21})_3P$, $(PhCH_2)_3P$, pyridine, picoline, or an alkylpyridine. Phosphine, phosphine oxides, and phosphites having the general formula $RR'PHO$, RR^1POR^2, and $RR^1POC(OH)R^2R^3$, where R, R′, R^1, R^2, and R^3 are C_1–C_{20} alkyls, are also used as ligands. Thus a mixture of C_{13} aldehydes and carboxylic acids in proportions of 10 : 1 has been obtained from dec-1-ene in the presence of $Co_2(CO)_8$ and $(C_8H_{17})_2POH$ (150 °C, 70 atm, H_2/CO = 1) for an overall degree of conversion of the olefin of 97%.[74]

Olefins can be carbonylated in a tubular reactor at 180 °C and a pressure of 170 atm in the presence of cobalt naphthenate.[75] The olefin is fully converted into carboxylic acid esters. When a mixture of CO with 5–10% of H_2 was used, the methyl esters of C_{13} acids were obtained in 97% yield from dodec-1-ene. They included 74% of the linear acid ester and the degree of conversion of the olefin was 63%.

Nickel complexes with tertiary amines, promoted by iodine compounds, are also effective catalysts of the carbonylation of α-olefins.[76] Thus the carbonylation of hexadec-1-ene in the presence of the $NiI_2-Py-HI$ system in an aqueous medium (88 atm CO, 200 °C) results in the formation of a mixture of C_{17} acids (yield 94%) containing 31.0% of acids with a linear structure. The remaining acids (47.0, 13.0, and 9.0%) contain methyl, ethyl, and propyl groups in the α-position, relative to the carboxy-group. Mixtures of saturated and unsaturated carboxylic acids, which can be used as surfactants after hydrogenation, have been obtained from cracking olefins.

Carboxylic acid esters are also synthesised by carbonylating olefins in the presence of mixtures of nickel and molybdenum or nickel and tungsten compounds, a halogen promoting agent, and a phosphorus- or nitrogen-containing base.[77] Treatment of ethylene with carbon monoxide in a medium consisting of a mixture of methanol and ethyl propionate in the presence of the $NiI_2-Mo(CO)_6-EtI$ system and PPh_3 (150–200 °C, 10–100 atm CO) affords methyl propionate in a high yield.

The selective synthesis of carboxylic acids or their esters has been achieved by carbonylating olefins in the presence of copper compounds with palladium, rhodium, ruthenium, iridium, or cobalt compounds in protic hydrogen halide acids.[78] The interaction of dec-1-ene with CO and methanol in the presence of $PdCl_2$, $CuCl_2$, and HCl under mild conditions results in the selective formation of methyl undecanoate.

Olefins are carbonylated in alcohols or phenols also under mild conditions (70–120 °C, 1–40 atm CO) in the presence of palladium complexes, phosphines, and peroxide compounds (H_2O_2, peracids). The presence of peroxides facilitates the coordination of the substrates to the palladium complexes and also promotes the oxidation of phosphines.[79]

The selectivity of the propene carbonylation process and the activity of Ru–Fe carbonyl clusters increase after the addition of $CuCl_2$ to the catalytic system. The main reaction products are methyl butyrate and butyric acid.[80]

Not only acids and their esters but also ketones can be obtained from olefins and CO. Diethyl ketone was formed from a mixture of C_2H_4, CO, and H_2O in the presence of the catalyst formed as a result of the rapid thermal decomposition of $Co_2(CO)_8$ on a carbon carrier at 150 °C and atmospheric pressure.[81]

Ketones have also been synthesised by carbonylating higher olefins (C_3–C_{20}) in a mixture with ethylene in the presence of H_2 on rhodium or cobalt catalysts at 150–250 °C and a pressure of 150 to 350 atm in various solvents, especially butanol.[82] The molar ratio of the catalyst and the mixture of ethylene with a higher olefin must be between 100 and 10 000 and that of the alcohol and the olefin must be between 0.3 and 2.0. Thus the interaction of ethylene and propene with CO in butanol at a pressure of 120 atm leads to the formation of a mixture of the ketones $EtCOCHMe_2$, PrCOEt, $(MeCH)_2CO$, $PrCOCHMe_2$, and Pr_2CO.

Ketones are also obtained by the reaction of olefins with CO and H_2O in the presence of cobalt carbonyl compounds and phosphines. For example, the reaction of C_3H_6 with CO and H_2O in the presence of $Co_2(CO)_8$ and $Ph_2PCH_2PPh_2$ at 165 °C and a pressure of 100 atm led to the formation of a mixture of the ketones Pr_2CO, $(Me_2CH)_2CO$, n-$PrCOCHMe_2$, and $PrCHO + Me_2CHCHO$.[83]

Homogeneous palladium catalysts deposited on polymers are active in the carbonylation of α-olefins. Thus the catalyst in the presence of which ethyl hexanoate was formed from pent-1-ene, styrene, and CO (120 °C, 28 atm CO) with 94% selectivity for an olefin conversion of 26.3% has been obtained from a copolymer of styrene with 1% of divinylbenzene (after bromination and treatment with $LiPPh_2$ in THF) by its interaction with $(PhCN)_2PdCl_2$.[84]

Palladium–anion exchanger catalysts, containing 0.4–0.75% of palladium on the Soviet produced anion-exchange resins AN-221, AN-251, and AN-511, possess a high activity, selectivity, and stability in the carbonylation of hex-1-ene.[85,86] Such catalysts can be used repeatedly (up to 10 times), retaining 0.35–0.4% of Pd under these conditions. Catalysts with a higher palladium content are less stable. Under optimum conditions (170 °C, 100 atm CO), C_7 acids are formed in an overall yield of 75–95%, the selectivity in the formation of oenanthic acid amounting to 50–60%.[86]

When $SnCl_2.2H_2O$ is added to palladium–anion exchanger catalysts (0.4% Pd/AN-221, 0.75% Pd/AN-511, and 0.4% Pd/AN-251) (atomic ratio Sn/Pd = 5–30), the selectivity in the formation of oenanthic acid increases to 94.5% with a simultaneous decrease the degree of conversion of the olefin to 30–35%.[86]

It has been suggested that the bimetallic complexes of $SnCl_2$ with chromium, molybdenum, or tungsten carbonyls can be used as catalysts of the carbonylation of olefins with formation of carboxylic acid esters (molar ratio 1–1.5 : 1, temperature 150–200 °C, CO pressure 250–300 atm).[87] These catalysts are less toxic than the nickel catalysts.

The carbonylation of isobutene or isobutyl alcohol in the presence of the $Rh(PR_3)_2X_2$ system, where X = Cl, Br, I, or another univalent anion and R = alkyl, aryl, or cycloalkyl, results in the selective formation of isovaleric acid. Such a reaction occurs, for example, in the interaction of iso-C_4H_8 with CO and H_2O at 18 to 20 °C and atmospheric pressure in the presence of $RhCl_2.[P(C_6H_{11})_3]_2$.[88] Palladium complexes with aminophosphine and phosphine ligands have been proposed as catalysts for the synthesis of isobutyric acid from propene, CO, and H_2O.[89] The process takes place selectively at 75–150 °C and a pressure of 20–350 atm. Isobutyric acid is formed in 79.5% yield from C_3H_6, CO, and H_2O in the presence of $Pd(OAc)_2$ and $(Me_2N)_3P$ in acetic acid and 38% HCl (110 °C, 315 atm).

The carbonylation of propene with formation of isobutyric acid and small amounts of n-butyric acid as well as a certain amount of $(CH_3)_2CHCl$ has been achieved on the $Pd(OAc)_2-Ph_3As-HCl$ catalyst at 75–150 °C and a CO pressure of 20–50 atm.[90]

The addition of n-Pr_3N to $Co_4(CO)_{12}$ increases the activity of the system in the hydrosilylation of α-olefins by a factor of 70 compared with the activity of $Co_2(CO)_8$.[91]

Isobutyric acid esters are obtained by carbonylating C_3H_6 in the presence of $Pd(PPh_3)_4$, PPh_3, and CF_3SO_3H (105 °C, 138 atm) in alcohol.[92]

Carboxylic acids and their esters are formed from C_{10}–C_{20} olefins or their mixtures in the presence of the $Co_2(CO)_8$–pyridine (or alkylpyridine) catalyst in C_2–C_{20} carboxylic acid at a pressure of 200 atm and a temperature of 150–200 °C.[93,94] The carbonylation is carried out in two stages. Initially the reaction is performed at 220 °C and the yield is then about 90%. The second stage, in which the yield of acids from the olefins is 10–12%, is performed at 180–190 °C. The fraction of linear acids formed in the first and second stages is 70–75% and 40–70% respectively. Water is added continuously to the reaction zone in order to increase the selectivity in the formation of linear carboxylic acids. In the carbonylation of a mixture of olefins, the contents of α-olefins in the first and second stages were 90 and 10.8% respectively. The carboxylic acids obtained are used in the manufacture of plastics, lubricants, and surfactants.

The carbonylation of π-olefins has been investigated[95–98] in the presence of homogeneous palladium catalysts at a low pressure of CO or the synthesis gas. The carbonylation of hept-1-ene on the $PdCl_2(PPh_3)_2-SnCl_2$ catalytic system in dioxan (185 °C, 20 atm, CO/H_2 = 1) takes place quantitatively with a selectivity of 85% in the formation of octanoic acid.[95]

In the carbonylation of non-1-ene in the presence of the $PdCl_2.(PPh_3)_2-PPh_3$ system in aqueous acetone (volume ratio acetone : water = 1 : 27, molar ratio olefin : Pd = 117, 13 atm, 90 °C, 6 h), the selectivity in the formation of capric acid increases to 88% with increase in the PPh_3/Pd ratio to 15. In the absence of PPh_3, the selectivity remains unchanged as the pressure is raised from 3 to 24 atm. The carbonylation products are a mixture of capric and α-methylpelargonic acid as well as a small amount (~4%) of α-ethylcaprylic acid.

The selectivity in the formation of linear acid increases when the CO pressure is reduced to 3 atm for the molar ratio PPh_3/Pd = 4.5.[96] With increase in the water concentration in acetone, the overall yield of carboxylic acid diminishes and the carbonylation process ceases with the volume ratio acetone : water = 3.

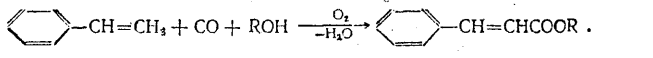
The influence of CO pressure on the carbonylation of non-1-ene is different in solution in the acetone–methanol mixture in the presence of the same $PdCl_2(PPh_3)_2$ catalytic system. With increase in the CO pressure from 7 to 24 atm and also with increase in the PPh_3/Pd ratio, the yield of methyl caprate also rises.[97]

The selectivity in the formation of octanoic acid from hept-1-ene in the presence of $PdCl_2(PPh_3).PR_3$ (where R = aryl or alkyl) in dioxan increases with increasing basicity of the phosphine ligand.[98]

The methyl esters of C_{12}–C_{17} carboxylic acids are obtained by carbonylating C_{11}–C_{16} olefins in methanol in the presence of the $Co_2(CO)_8$–pyridine–isoquinoline catalytic system at 140 °C and a CO pressure of 250–300 atm.[99] Thus methyl dodecanoate has been obtained with a selectivity of 93% from undec-1-ene, CO, and CH_3OH (140 °C, 300 atm). Cobalt carbonyl compounds are removed from the reaction products by oxidising them with oxygen or air in the liquid phase at a pressure of 3 atm and a temperature of 50 °C.

Higher C_{10}–C_{20} carboxylic acids are obtained by carbonylating C_9–C_{19} olefins under the same conditions using the catalysts described by Katsnel'son and Bel'nik.[99] The processes are carried out in a solvent with vigorous stirring of the reaction mixture.[100]

The synthesis of cinnamic acid esters by the oxidative carbonylation of styrene has been described:[101–106]



The catalysts used are 2% Pd/C[101,102] as well as Pd, Pt, Rh, Ir, Ru, and Os compounds or their mixtures with Cu^{2+} and Fe^{2+}.[103,104] Tertiary amines or bases—alkali or alkaline earth metal salts of organic or inorganic acids—are also used as additives. Aluminium powder[105] and aliphatic polyamines—ethylenediamine, piperazine, etc.[106]—can be added to compounds of the platinum group metals.

Cinnamic acid esters, which are widely used in the manufacture of medicinal drugs and perfumes, plant protecting agents, and light-sensitive resins, are obtained from styrene at CO and O_2 partial pressures ⩽18 atm and ⩽7 atm respectively in alcohol at 120 to 170 °C.[105] The yield of the target products is between 26 and

82.4% for a degree of conversion of styrene from 35 to 75.8%. La, Nd, Ce, Eu, V, and Pr oxides and acetates are effective process cocatalysts. The Pd : Cu (or Pd : Fe) atomic ratios range from 1 : 10 to 1 : 30, while the Cu : Ln (or Fe : Mn) atomic ratios are between 1 : 0.1 and 1 : 50.[105]

The carbonylation of styrene in the presence of the complex $PdCl_2.(PPh_3)_2$ in dioxan results in the formation of α-phenylpropionic acid with a selectivity of 99% for a degree of conversion of the olefin amounting to 93%. The replacement of carbon monoxide by the synthesis gas does not alter the overall yield of carboxylic acids but it does induce an increase in the process selectivity in the direction of the formation of β-phenylpropionic acid.[107]

An improved method has been proposed for the carbonylation of α-olefins, which makes it possible to obtain carboxylic acids or their ester with an increased content of linear products at 80–120 °C.[108] For this purpose, one uses palladium–sulphonic acid catalysts with phosphines, containing added perfluorosulphonic acids (CF_3SO_3H, $C_2H_5SO_3H$, $C_4H_9SO_3H$, and $C_8H_{17}SO_3H$) and polymeric perfluorosulphonic acids having molecular weights in excess of 5000, as promoting agents. Thus the carbonylation of propene in methanol in the presence of $Pd(PPh_3)_4$, PPh_3, and the additive CF_3SO_3H (molar ratio Pd/CF_3SO_3H = 1/2, 105°, 138 atm, CO, 2 h) results in the formation of methyl esters of butyric acids in 53.4% yield. The selectivity in the formation of the n-butyric acid ester is 69.2%. An increase in the amount of the CF_3SO_3H additive increases the degree of conversion of propene into butyric acid esters to 92.5%.

α-Olefins or diolefins are hydrocarboxylated under mild conditions in the presence of $PdCl_2-CuCl_2$ and O_2 in alcohol to which gaseous HCl has been added.[109] Mainly esters of branched carboxylic acids are formed. Olefins with an inner double bond afford carboxylic acid esters branched at the carbon atom which is closer to the end of the carbon chain. Thus $CH_3O_2CCH(CH_3)(CH_2)_4CH(CH_3)CO_2CH_3$ is formed quantitatively from octa-1,7-diene. Cyclic olefins also readily enter into the carbonylation reaction .[109]

Catalytic systems based on $Co_2(CO)_8$ and alkylpyridines (with the exception of pyridines having an *ortho*-substituent) capable of carbonylating selectively olefins with an inner double bond (for example, dodecenes) to form linear carboxylic acids have been devised.[110,111] Under the reaction conditions (180 °C, ratio of promoting agent and catalyst 10 : 1, 180 atm CO), the initial olefins with an inner double bond isomerise to α-olefins, which are in fact carbonylated. The initial α-olefins are obtained by the dehydrochlorination of the chlorinated paraffins. The process can be carried out in the presence of paraffins (up to 75%) and carbon monoxide containing up to 10% of H_2. The cobalt catalyst is normally employed as the acetate, naphthenate, 2-ethylhexanoate, or stearate, which are converted into cobalt carbonyl, while the promoting agents are β- or γ-picolines, 3,4- or 3,5-lutidines, or ethylpyridines in an amount of 3–25 moles per mole of the cobalt compound. Thus the carbonylation of a mixture of dodecenes in the presence of cobalt naphthenate and γ-picoline (molar ratio 1 : 10) in methanol (180 °C, 180 atm CO, 2% H_2 in CO) leads to the formation of a mixture of methyl esters of tridecanoic acids in 60% yield and a selectivity with respect to the linear isomer of 74%. Cobalt carbonyl is removed from the reaction products by treatment with air at 40–60 °C, cobalt oxides being isolated and returned to the cycle. The process is carried out under continuous conditions.[111]

The selective hydromethoxycarbonylation of higher olefins takes place with a high molar ratio of alkylpyridines and the cobalt catalyst (10–100). Otherwise there is a sharp increase in the yield of branched carboxylic acid esters. The productivity of the catalytic systems described above is 300–500 g of the ester per litre of the reaction solution per hour. Calculations have demonstrated the economic efficiency of the given method of synthesis of esters and acids having a linear structure.[112]

In order to reduce the yield of high-boiling products, it has been suggested either to remove water from the initial reactants by azeotropic distillation[113] or to replace the large amount of alkylpyridines by high-boiling residues isolated after distilling off the reaction products.[114] It has been suggested that the selective methoxycarbonylation of α-olefins and alkylenenitriles be carried out in the presence of cobalt catalysts with added ruthenium compounds and tertiary nitrogen-containing bases.[115] Hex-1-ene is selectively converted into methyl oenanthate in methanol in the presence of $Co_2(CO)_8$, isoquinoline, and $Ru_3(CO)_{12}$.

Dialkyl ketones can be obtained from ethylene (or propene), CO, and H_2 in the presence of the $Pd(OAc)_2-PPh_3$ catalytic system under mild conditions (30–70 °C, 1 atm) in aqueous trifluoroacetic acid.[116] Butyric acid, butyraldehyde, paraffins, and CO_2 are formed in small amounts. The rate of reaction and the isomeric composition of dialkyl ketones depend on the concentration of water in the reaction mixture. For a water content less than 5 vol. %, a mixture of 2,4-dimethyl-3-pentanone, 2-methyl-3-hexanone, and 4-heptanone is formed in proportions of 1 : 2 : 1. At a water concentration of 25–30 vol. %, the above ratios change to 1 : 5 : 1. It has been suggested that the ketones are synthesised via the intermediate formation of the Pd–H hydride complexes, formed as a result of the heterolytic capture of hydrogen by the palladium complex.

A method has been proposed for the carbonylation of olefinic compounds under mild conditions in the presence of a cobalt catalyst and disubstituted phosphines RR′ – PH as promoting agents.[117] The catalytic system is separated from the reaction products (acids or esters) by distilling off the latter.

Pent-3-enoic acid esters, which are intermediates in the synthesis of adipic acid diesters, are synthesised from butadiene, CO, and alcohols in the presence of $Co_2(CO)_8$ promoted by pyridine, quinoline, isoquinoline, both unsubstituted and substituted C_1-C_6 alkyls or alkenyls, aryls, and C_7-C_{10} arylalkyls or alkylaryls.[118] The process is carried out in the presence of the polymerisation inhibitors Ph_2NH, (Ph)(Me)NH, *NN*′-tetraethyl-*p*-phenylenediamine, *NN*′-di-β-naphthyl-*p*-phenylenediamine, benzoquinone, anthraquinone, or chloramine. Thus methyl pent-3-enoate is formed with a selectivity of 98.5% from butadiene, CO, and methanol in the presence of $Co_2(CO)_8$, pyridine, and *NN*′-di-β-naphthyl-*p*-phenylenediamine (120 °C, 300 atm CO, 1.5 h). The degree of conversion of the diolefin reaches 99.5%.

In the presence of the $PdCl_2$ catalyst, the carbonylation of a disubstituted but-2-ene proceeds with formation of the diester of an unsaturated C_6 dicarboxylic acid:

$$RCH_2CH{=}CHCH_2R + CO \rightarrow RCOCH_2CH{=}CHCH_2COR\ ;$$
$$R = OAc,\ OMe,\ OH \text{ or } Cl.$$

The selectivity of the reaction increases in the presence of polar and non-basic solvents.[119]

Dicarboxylic acid esters are obtained by treating unsaturated C_5-C_{15} carboxylic acids with carbon monoxide in the presence of C_1-C_3 alcohols using as the catalyst cobalt carbonyl with added water (up to 50% of the alcohol) and alkanes to separate the reaction products from the catalyst. Thus the interaction of the methyl ester of tricyclo[5.2.1.$0^{2,6}$]dec-3(or 4)-ene-8(or 9)-carboxylic

acid with CO (100 atm, 160 °C) in the presence of $Co_2(CO)_8$ in aqueous methanol with added cyclohexane results in the formation of dimethyl ester of tricyclodecanedicarboxylic acid in 79.3% yield.[120]

Together with olefins, other unsaturated compounds enter into the carbonylation reaction. A series of processes involving the carbonylation of unsaturated alcohols with formation of lactones[121] in the presence of $PdCl_2$, CO, O_2, and concentrated HCl in dry THF at room temperature and atmospheric pressure have been described. For example, but-3-enol is converted in 60% yield into α-methyl-γ-butyrolactone, while 2-methylbut-3-en-1-ol is converted into a 2:1 mixture of *trans*- and *cis*-2,3-dimethyl-γ-lactones. Pent-4-en-1-ol is converted into α-methyl-δ-valerolactone in 75% yield. In the presence of $Co_2(CO)_8$, the corresponding lactones are formed from saturated alcohols in yields ranging from 3 to 51%. The process takes place under fairly severe conditions—at 240 °C and a CO pressure of 900 atm.

Succinic acid diesters have been obtained by carbonylating acrylic acid esters in the presence of cobalt-containing catalysts and pyridines. Thus the interaction of methyl acrylate with CO and methanol in the presence of $Co_2(CO)_8$–Py in toluene (130 °C, 120–130 atm CO) affords dimethyl succinate in 94.2% yield. Dibutyl and dicyclohexyl succinates are obtained analogously in 91.2 and 90.0% yields respectively.[122]

In the methoxycarbonylation of 3-(β-cyanoethoxy)propene (110–120 °C, 200 atm CO) in the presence of $Co_2(CO)_8$, the addition of pyridine and CH_3ONa does not affect the rate of reaction or lower it.[123] The selectivity in the formation of methyl 4-(β-cyanoethoxy)butyrate then increases from 52 to 60–70%, while the selectivity in the formation of methyl 3-(β-cyanoethoxy)-isobutyrate rises from 1.7 to 3.3%. The addition of $PdCl_2$ to $Co_2(CO)_8$ in the absence of pyridine increases the rate of reaction by a factor of 10, while in its presence the increase is by a factor of 15–17. The addition of $PdCl_2$ has a similar effect on the carbonylation of propene in the presence of pyridine (140–160 °C, 200 atm CO). The introduction of up to 7.5% of H_2 into carbon monoxide acts effectively on the carbonylation process. The addition of $PdCl_2$ to $Co_2(CO)_8$ also influences the carbonylation of acetonitrile [140 °C, 200 atm CO, $Co_2(CO)_8$–pyridine mixture in proportions of 1:2]: an increase in the degree of conversion of acetonitrile from 28 to 80% is observed with the simultaneous rise in the yields of methyl γ- β-, and α-cyanobutyrates from 18.0, 3.4, and 4.9% to 52.0, 8.8, and 17.0% respectively.[123]

The carbonylation of CN-containing olefinic hydrocarbons with formation of the esters of the corresponding carboxylic acids has been described.[124–128] The esters are used for the synthesis of aminoacids, which have found extensive application in industry, agriculture, medicine, and biology. Complexes based on cobalt, palladium, and ruthenium are effective catalysts. Thus the carbonylation of acetonitrile in the presence of cobalt or ruthenium carbonyls and polyamines [poly(vinylpyrrolidinone)] as ligands leads to the formation of methyl α-cyanopropionate in 55.4% yield.[124]

The cobalt catalysts are promoted by γ-picoline oxide[125] and also by the oxides of various substituted pyridines.[126] The substituents can be not only alkyl or hydroxyalkyl groups but also the $(CH_2)_nCN$, $(CH_2)_mOR$, $(CH_2)_fCOOH$, or $(CH_2)_pCOOR$ groups.[125] Not only pyridine oxides but also phosphine oxides, sulphide oxides (sulphoxides?), or sulphones are effective ligands.[126] Unsaturated compounds are carbonylated in nitriles or dinitriles. The carbonylation of acetonitrile (97.5 °C, 70 atm, $CO/H_2 = 1$) in the presence of $Co_2(CO)_8$ and γ-picoline oxide in adipodinitrile with added CH_3OH resulted in a degree of conversion of 84.4%, the mixture of products consisting of 97.5% of methyl γ-cyanopropionate.[127,128] The catalytic system is extracted from the reaction mixture with a fourfold excess of C_5–C_8 alkanes and is returned to the reaction cycle.

A method has been proposed for the selective synthesis of isobutyric acid by carbonylating propene in the presence of a catalytic system containing palladium(II) compounds as well as arsenic compounds in the inorganic aicds HBr, HCl, H_2SO_4, HI, H_3PO_4, or HBF_4.[129] When propene is carbonylated in an autoclave with glass-lined walls (105 °C, 60 atm CO, 1.5 h) in the presence of $Pd(OAc)_2$, $AsPh_3$, and HCl (molar ratios 1:40:90) in aqueous isobutyric acid, isobutyric acid is formed with a selectivity of 74.9% for a 100% conversion of the olefin.

δ-Cyanovaleric acid esters are obtained in 75% yield by carbonylating 3-cyanobut-1-ene in alcohol and acetone (160 °C, 200 atm CO) in the presence of the $Co_2(CO)_8$–pyridine catalytic system.[130]

The carbonylation of acetonitrile in the presence of $Co_2(CO)_8$ with formation of methyl α-cyano-α-methylacetate and β-cyanopropionate (120–140 °C, 260–300 atm, $CO/H_2 = 8$–10) has been described.[131] Their hydrolysis affords respectively methylmalonic and succinic acids. The cyanoethylation of methyl α-cyano-α-methylacetate gives rise to $NCC(COOCH_3)(CH_3)CH_2CH_2CN$, which is hydrolysed to α-methylglutaric acid. The hydrogenation of the β-cyanopropionic acid ester results in the formation of α-pyrrolidinone in 95–98% yield. The reactions proceed in accordance with the following schemes:

$$NCCH{=}CH_2 + CO + CH_3OH \xrightarrow{Co_2(CO)_8,\ H_2} \begin{cases} \longrightarrow NCCH(CH_3)COOCH_3 \xrightarrow{H_2O} NH_3 + \\ \quad + HOOCCH(CH_3)COOH + CH_3OH + CO_2, \\ \quad \alpha\text{-methylmalonic acid} \\ \longrightarrow NCCH_2CH_2COOCH_3 \xrightarrow{H_2O} NH_3 + \\ \quad + HOOCCH_2CH_2COOH + CH_3OH; \\ \quad \text{succinic acid} \end{cases}$$

$$NCCH(CH_3)COOCH_3 + NCCH{=}CH_2 \rightarrow NCC(COOCH_3)(CH_3)CH_2CH_2CN \xrightarrow{H_2O} \rightarrow 2NH_3 + 2CO_2 + HOOCCH(CH_3)CH_2CH_2COOH;$$

α-methylglutaric acid

$$NCCH_2CH_2COOCH_3 \xrightarrow[150\text{–}300^\circ C\ 2\text{–}21\ atm]{H_2,\ NH_3} \begin{array}{l} H_2C\text{—}CH_2 \\ | \quad\quad | \\ H_2C \quad NH \\ \diagdown \quad \diagup \\ \quad CO \end{array}$$

α-pyrrolidinone

Methyl 5-cyanovalerate has been obtained with a selectivity of 92% for a conversion of the initial compound of 92% by carbonylating *cis*-pent-2-enylnitrile in the presence of $Co_2(CO)_8$ (180 °C, 310 atm) in a mixture of tetramethylene sulphone and methanol.[132]

α-Acyloxypropionic acids, whose hydrolysis affords lactic acid, are formed from the vinyl esters of carboxylic acids in the presence of $Pd(PR_3)_4$ in an excess of PR_3 (R is an aromatic group).[133] A characteristic feature of the process is a rigorously specified amount of water necessary for the formation of the product, its concentration in the mixture amounting to about 1.0 wt.%. The carbonylation of vinyl acetate (150 °C, 49 atm CO, H_2O concentration 0.9%) in the presence of $[(CH_2{=}CHCH_2)PdCl]_2$ and PPh_3 in butyric acid results in the formation of α-acetoxypropionic acid with a selectivity of 67% for 96% conversion of vinyl acetate.[133]

The carbonylation of alkenyl alkyl carbonates in the presence of palladium complexes leads to the formation of the alkyl esters of βγ-unsaturated carboxylic acids.[134] The reaction takes place in accordance with the equation

$$R^1R^2C{=}CR^3CR^4R^5OC(O)OR \xrightarrow[-CO_2]{CO} R^1R^2C{=}CR^3CR^4R^5COOR\ .$$

The catalysts employed are $Pd(PPh_3)_2(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ in an inert solvent (alcohol, THF) or in its absence. The interaction of methyl 2-propenyl carbonate with carbon monoxide (100 °C, 70 atm CO) in the presence of $Pd(OAc)_2$ and PPh_3 affords a quantitative yield of methyl but-3-enoate.[134]

An analogous procedure is used to obtain methyl pent-3-enoate from but-2-enyl methyl carbonate, ethyl hept-3-enoate from ethyl hex-2-enyl carbonate and methyl 4,8-dimethylnona-3,7-dienoate from butadiene.[124]

Effective methods have been proposed for the carbonylation and regeneration of cobalt–pyridine catalysts used for the synthesis of polyol esters of carboxylic acids from C_3–C_{30} α-olefins (180–185 °C, 200 atm CO).[135–137]

The $Co_2(CO)_8$–isoquinoline complex in an aromatic hydrocarbon and alcohol is used successfully for the synthesis of methyl pent-3-enoate from butadiene.[138,139] Thus methyl pent-3-enoate has been obtained in a high yield from butadiene and carbon monoxide (containing 3% of H_2) in a mixture of benzene, isoquinoline, and methanol (123 °C, 300 atm CO) in the presence of $Co_2(CO)_8$. The catalyst is regenerated by the stepwise distillation of benzene, isoquinoline, methanol, and methyl pent-3-enoate from the reaction mixture. After treating the residue with aqueous solutions of inorganic acids (HCl, HNO_3, H_2SO_4—5% excess relative to cobalt), cobalt carbonate is precipitated with an aqueous Na_2CO_3 solution.

A method has been proposed for the synthesis of dicarboxylic acid esters, including adipic acid ester, by carbonylating unsaturated acid esters[140,141] under conditions analogous to those described in patents.[138,139] The carbonylation of methyl but-2-enoate in methanol and isoquinoline in the presence of $Co_2(CO)_8$ (160 °C, 200 atm, CO containing 0.7% of H_2) gives rise to a 77.9% yield of unsaturated acid esters consisting of 77% of $(CH_2)_3(COOMe)_2$, 18% of the $MeOCOCH_2CH(Me)COOMe$–$MeOCOCH(Et)COOMe$ mixture and 5% of $C_7H_{17}COOMe$. The esters of other dicarboxylic acids, mainly with a linear structure, are obtained similarly in a high yield.[141] Dimethyl adipate has been obtained in 81.8% yield from methyl pent-3-enoate, CO, and methanol, the content of the pentanoic acid ester in mixture not exceeding 3.8%.[142]

The carbonylation of methyl pent-3-enoate in aromatic hydrocarbons under conditions such that the ratio of the tertiary nitrogen-containing base and the cobalt compound is between 2 and 25 leads to the formation of dimethyl adipate in 96.3% yield.[143] Dimethyl adipate has been synthesised in 70.5% yield from methyl pent-3-enoate by the method involving carbonylation in the presence of CoS and tertiary amines (185 °C, 200 atm CO). CoS is then readily isolated and can be reused.[144]

A method has been proposed for the synthesis of succinic acid esters from C_2H_4, CO, and alcohol in the presence of platinum group metal complexes with added iron, copper, and cobalt salts and aminoacids such as glycine, alanine, valine, phenylalanine, etc.[145] For example, dimethyl succinate is formed from a 1 : 1 mixture of C_2H_4 and CO at an overall pressure of 80 atm ($PdCl_2$, glycine, 100 °C) in methanol. Double carbonylation of ethylene takes place during the reaction:[146]

$$CH_2{=}CH_2 + 2CO + 2CH_3OH \rightarrow \begin{matrix} CH_2COOCH_3 \\ | \\ CH_2COOCH_3 \end{matrix}.$$

(b) Carbonylation of olefins in the presence of acid catalysts. The use of organic or inorganic acids or acid complexes as catalysts makes it possible to obtain products branched in the α-position relative to the functional group by carbonylating unsaturated compounds (olefins, dienes).[1,3] The carbonylation is usually carried out at temperatures in the range 20–125 °C and CO pressures up to 200 atm. The catalysts are H_2SO_4, HF, H_3PO_4, $AlCl_3$, SbF_5, HSO_2Cl, FSO_2Cl, BF_3, $BF_3.n\,ROH$, $BF_3.n\,H_2O$, $BF_3.n\,RCOOH$ (n = 1 or 2), etc.[147–153]

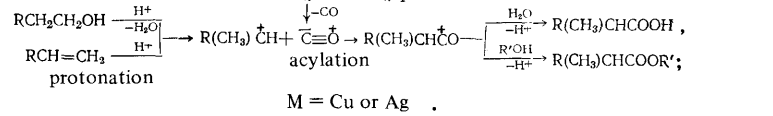
C_{20}–C_{24} α-olefins or their mixtures are carbonylated in concentrated H_2SO_4 at 10–35 °C and a CO pressure of 35–140 atm.[147] Before being supplied to the reactor, the olefins are fused, but the temperature in the reactor is maintained below the melting point of the olefin, which makes it possible to increase the contact time between the olefin and the catalyst and to raise the process selectivity. Thus, when eicos-1-ene heated to 45 °C under a CO pressure of 94 atm is added gradually to vigorously stirred concentrated H_2SO_4, a C_{21} acid is formed in 82.1% yield.

For the molar ratios of H_2SO_4, ethyl formate, and 1-hexanol of 10 : 4 : 1, the overall yields of the ethyl esters and acids in the synthesis products are influenced by the temperature, reactant ratio, and the H_2SO_4 concentration. Mainly ethyl esters of 1-methylcyclopentanecarboxylic and cyclohexanecarboxylic acids are formed from cyclohexanol.[150] The overall yield of the esters and acids obtained in proportions of 2–3 : 1 was 65–75%.

The carbonylation of branched and linear olefins (2-methylbut-2-ene, 2-methyl-pent-2-ene, mixtures of di- and tri-isobutenes, and also hex-1-ene and hept-1-ene) in the presence of BF_3–H_2O and ethyl formate at atmospheric pressure and a temperature of 20–90 °C results in the formation of the ethyl esters of the corresponding acids and directly the acids themselves in an overall yield ranging from 50 to 90%. At the optimum carbonylation temperature of 50 °C, the maximum yields of the ethyl esters of the acids and of the acids themselves obtained from hex-1-ene and hept-1-ene were 51 and 50% respectively.[151]

The corresponding carboxylic acids have been obtained in yields of 45–85% by the carbonylation of C_6–C_{12} iso- and n-olefins with carbon monoxide at 30 °C and atmospheric pressure in the presence of the 97% H_2SO_4 + Ag_2O (or Cu_2O) and $(BF_3.H_2O)(BF_3.H_3PO_4)$ + Cu_2O catalytic systems.[152]

The mechanism of the carbonylation of olefins and alcohols in the presence of the above catalysts has been investigated.[153] The activity of the catalysts increases with increase in their Hammett acidity (H_0): $BF_3.H_2O$ (−11.40) > H_2SO_4 (−10.65) > $(BF_3.H_2O)$. $(BF_3.H_3PO_4)$ (−10.00) > H_3PO_4 (−5.18). The reactivity of olefins with the normal structure is lower than that of branched olefins and the selectivity in the formation of carboxylic acids or their esters is higher for linear α-olefins. The reactivity of alcohols increases on passing from primary to secondary and then to tertiary alcohols. The yields of carboxylic acids are maximum at the optimum rates of the stages involving the protonation of the substrates and the addition of CO to the carbonium ions formed (the acylation stage). This conclusion is valid also when the carbonylation of olefins and alcohols is carried out in the presence of the H_2SO_4, $BF_3.H_2O$, and $(BF_3.H_2O)(BF_3.H_3PO_4)$ catalysts with added Cu_2O and Ag_2O. The carbonylation proceeds in accordance with the scheme:



The protonation of the substrates is ensured by the presence of the acid component and CO is activated by the intermediate formation of Cu(I) or Ag(I) carbonyls during the process. When

ethyl formate is used as the carbonylating agent, carbon monoxide is activated in the stage involving the decomposition of ethyl formate with formation of CO *in situ*.

The carbonylation of propene in the presence of $BF_3.CH_3OH$ (50 °C, 60 atm) results in the formation of mainly methyl isobutyrate with a small amount of methyl dimethylvalerate and methyl neodecanoate.[154] The complex $BF_3.CH_3OH$ with added Cu_2O or Ag_2O is an effective catalyst of this process. When diisobutene is carbonylated by carbon monoxide under pressure, the esters of C_6–C_{11} acids are formed in high yields.[155] Methyl isobutyrate is formed analogously from C_3H_6, CO, and H_2O in the presence of $BF_3.(CH_3)_2CHCOOCH_3$, $BF_3.CH_3OH$, and $BF_3.H_2O$.[156]

One of the most important target products of the carbonylation of olefins in the presence of acid catalysts is isobutyric acid or its esters—the intermediates in the synthesis of acrylic acid or methyl methacrylate.

When a mixture of methanol, methyl isobutyrate, and Cu_2O is used in molar proportions of 31.2 : 97.5 : 1 in the presence of BF_3 (50 °C, 49 atm CO) with subsequent supply of propene into the reactor, methyl isobutyrate is obtained in 99% yield.[157]

Propene is carbonylated in the presence of a 15-fold excess of HF (30 °C, 340 atm CO, 30 min), after which HF is distilled off and directed to the carbonylation stage.[158,159] The isobutyric acid fluoride obtained is hydrolysed (with an acid fluoride : water molar ratio of 1 : 0.2–0.4) at –40 °C in the presence of NaF as the HF acceptor. $NaHF_2$ is separated by centrifugation from the resulting equilibrium mixture of the isobutyric acid anhydride, its fluoride, and $NaHF_2$. The acid fluoride is returned to the hydrolysis stage and $NaHF_2$ is decomposed into NaF and HF, which are directed respectively to the hydrolysis and carbonylation stages. The selectivity in the formation of isobutyric acid anhydride is close to 100%.

Isobutyric acid fluoride is obtained by carbonylating isopropyl chloride in the presence of an excess of HF (20–80 °C, 50 atm CO), after which the product is hydrolysed with water to form isobutyric acid:[160]

$$(CH_3)_2CHCl + CO \rightarrow (CH_3)_2CHCOF \xrightarrow{H_2O} (CH_3)_2CHCOOH + HF.$$

A continuous method has been developed for the synthesis of acid fluorides, in particular isobutyryl fluoride, from C_3H_6, CO, and HF via their effective mixing in a turbulent mixer (30–80 °C, 196 atm CO).[161] The degree of conversion of C_3H_6 reaches 100% and the selectivity in the formation of isobutyryl fluoride is about 90%.

Isobutyric acid can be obtained in 98% yield by the isomerisation of isopropyl formate in the presence of HF:[162]

$$HCOOCH(CH_3)_2 \xrightarrow{CO,\ HF} (CH_3)_2CHCOOH.$$

A method has been proposed for the synthesis of isobutyric acid and its esters by carbonylating propene in an autoclave with a high-speed stirrer in the presence of not more than 2 mol % of alcohol or water in the reaction mixture.[163] The molar ratios H_2O (alcohol) : C_3H_6 : HF : CO = 0.96 : 1 : 10 : 1.5. The process is carried out under continuous conditions at 100–140 °C and a pressure of 80–140 atm. It takes place in the liquid phase and the reaction products (isobutyric acid fluoride and isopropyl isobutyrate) are readily isolated and the mixture is expanded to give a pressure of 1–4 atm. HF, isopropyl fluoride, isopropyl alcohol, and diisopropyl ether are then transferred to the gas phase and are returned to the process. Isobutyric acid fluoride and isopropyl isobutyrate are hydrolysed, HF and isopropyl alcohol are returned to the cycle, and isobutyric acid is purified further by double fractionation. The overall yield of the acid exceeds 90% and the selectivity in its formation is 93%.

An improved version of this process has also been proposed.[164] The reaction is carried out at 70 °C and 120 atm CO, the residence time of propene in the reactor amounting to 5 min. For a molar ratio C_3H_6 : HF = 1 : 20, the yield and selectivity in the formation of isobutyric acid fluoride reach respectively 95 and 96.5%. A characteristic feature of this process is that the carbonylation of C_3H_6 or iso-BrF are carried out in a polyhalogenoalkane (it is best to use 1,1,2,2-tetrachloroethane) with formation of a two-phase system with HF. A method has been proposed for the preparation of isobutyric acid fluoride by passing a mixture of HF, CO, and C_3H_6 (in molar proportions of 40 : 13 : 1) through a tubular reactor (35.7 atm, 20 °C) with a contact time of 1–2 min.[165–167] The yield of isobutyric acid fluoride is then 90%.

Carboxylic acids can be obtained by carbonylating olefins in the presence of the $HF : BF_3 : H_2O$ = 5.1 : 1 : 1.1 catalytic system at 60 °C and a pressure of 7.5 atm.[168]

Contact between the reactants is achieved by means of a stirrer rotating at 1000 rev min^{-1}. This method is suitable for the carbonylation of alcohols. Under the conditions indicated, trimethylacetic acid is formed in 88% yield from isobutyl alcohol after 45 min.

The reaction of C_3H_6, CO_2, and CH_3OH in the presence of $RuCl_2(PPh_3)_2$ (CO_2 pressure 45 atm at 20 °C, reaction temperature 215 °C, 20 h) in acetone results in the formation of a 1 : 1 mixture of methyl isobutyrate and methyl butyrate in 32% yield:[169]

$$C_3H_6 + CO_2 + CH_3OH \rightarrow \begin{cases} (CH_3)_2CHCOOCH_3, \\ CH_3CH_2CH_2COOCH_3. \end{cases}$$

Aromatic hydrocarbons have been carbonylated on the HF–BF_3 catalyst with formation of aldehydes.[170] Ethylbenzene, cumene, xylene, mesitylene, diisopropylbenzene, biphenyl, naphthalene, bibenzyl, isobutylbenzene, tetralin, and toluene can be carbonylated by this method. Under mild conditions (20 °C, 10–15 atm), *p*-toluic aldehyde was obtained selectively in 98% yield from toluene and CO in the presence of the HF–BF_3 catalytic system in apparatus made of copper alloys. A non-specific method of carrying out the process has been developed.

Carboxylic acids branched in the αα-positions, obtained by the method described above, have found extensive applications in the preparation of synthetic lubricants distinguished by high chemical and thermal stabilities,[171] as detergents, corrosion inhibitors,[172] insecticides, perfumes, preservatives, and antifungal preparations.[173]

III. Carbonylation of alcohols

Many valuable chemical products, which have found extensive applications in industry, agriculture, and medicine, can be obtained by carbonylating alcohols. A wide variety of compounds have been obtained from the simplest alcohol (methanol) depending on the process conditions and the catalyst used:

$$CH_3OH \rightarrow \begin{cases} \xrightarrow{CO,H_2} CH_3CHO,\ CH_3CH_2OH,\ HO(CH_2)_nCH_3,\ HO(CH_2)_nOH, \\ \xrightarrow{CO} CH_3COOH,\ CH_3COOCH_3,\ (CH_3)_2O, \\ \xrightarrow{CO} HCOOCH_3 \rightarrow HCOOH. \end{cases}$$

The likely usefulness of the processes involving the carbonylation of alcohols is confirmed by the widespread industrial use of the method of synthesis of acetic acids from methanol in the presence of a rhodium catalyst developed by the Monsanto Company:[1,3]

$$CH_3OH + CO \rightarrow CH_3COOH .$$

In the future, it will be possible to synthesise glycols (ethylene glycol) from CO and H_2, to prepare ethanol by introducing an extra CH_2 group into methanol, etc. The number of publications concerned with the study of the reactions involving the conversion of alcohols, acids, esters, and olefins into higher homologues by the interaction of the latter with CO and H_2 has been increasing. The prospects for the employment of alcohol carbonylation reactions can be inferred from the relevant publications.[174-180]

The available information about the carbonylation of methanol and some of its homologues and derivatives under the conditions of homogeneous and heterogeneous catalysis will be examine below.

In recent year, much attention has been devoted not only to the creation of catalysts but also to the elucidation of the mechanisms of the alcohol carbonylation reactions.[179,180] The most effective catalysts of the carbonylation of methanol with formation of acetic acid are rhodium complexes. Cobalt compounds are less selective and less active. Rhodium complexes with monodentate ligands are less active than those with bidentate ligands. The bidentate complexes exhibit a reduced activity in the initial stage of the process. The identical rates of carbonylation attained when $RhCl_3$ and phosphine complexes of Rh^+ are used indicate the similarity of the nature of the catalytically active species formed from the above compounds during the process.[180]

It has been suggested that rhodium complexes are more selective than catalytic systems based on iridium.[181] Selectivity in the formation of acetic acid on carbonylation of methanol in the presence of rhodium systems approaches 99%. When iridium catalysts are used, the selectivity does not exceed 90%, which is associated with the occurrence of side reactions involving the formation of methane:

$$CH_3OH + CO \rightarrow CH_4 + CO_2 ,$$
$$CH_3OH + H_2 \rightarrow CH_4 + H_2O .$$

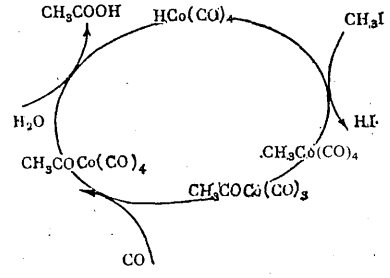
Their contribution increases at high carbon monoxide pressures and for a low water content in the system. An increase in the I^- and H_2O concentrations promotes the water gas conversion reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 .$$

In the presence of a rhodium catalyst, the degree of conversion of CO via this reaction hardly exceeds 10%.

When rhodium and iridium catalysts are used, the CH_3I promoting agent plays an especially important role. The rate of carbonylation of methanol is proportional to the CH_3I and rhodium concentrations and is independent of the concentrations of methanol, carbon monoxide, and acetic acid. For the iridium complexes, the rate of reaction is described by a more complex relation and is determined to a large extent by the composition of the catalytic system and the process conditions. The rate-limiting stage of the process in the presence of the rhodium and iridium catalysts is the oxidative addition of CH_3I to the catalytically active species $[Rh(CO)_2I_2]^-$ and $[Ir(CO)_2I_2]^-$ respectively.[181]

Cobalt catalysts are less selective in the carbonylation of methanol because the cobalt carbonyl hydride $HCo(CO)_4$, responsible for catalysis, catalyses in addition also side reactions: the conversion of methanol into ethanol by the addition of the CH_2 group, the water gas reaction, esterification, etc., which reduces sharply the process selectivity.[181] The catalytic cycle in the methanol carbonylation process in the presence of a cobalt catalyst is presented schematically below:[182]



In the carbonylation reactions of alcohols and esters, Ru, Ni, Pd, Pt, Fe, and Cu compounds also exhibit activity.[182]

The use of CH_3Br instead of CH_3I as the agent promoting the rhodium catalyst reduces the rate of carbonylation of methanol with formation of acetic acids by a factor of ~ 10.[181]

A coupled process involving the carbonylation of mixtures of methanol and ethylene with formation of a mixture of acetic and propionic acids has been patented.[183] The process is carried out in the presence of an industrial catalytic system which inlcudes $RhCl_3$, HI, and CH_3I. The reaction takes place at 185 °C and a CO pressure of 2 atm. The rate of formation of acetic acid is described by the equation

$$r = 5 \cdot 10^{10} e^{-7630/T} [Rh] [I^-] \text{ mol AcOH litre}^{-1} \text{ h}^{-1},$$

where [RH] and $[I^-]$ are the concentrations of rhodium and I^- in solution.

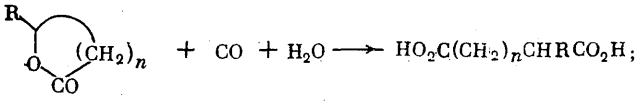
Cobalt and iron clusters having the general formulae $M[FeCo_3.(CO)_{12}]$ or $M[CoFe_3(CO)_{13}]$, where M is a hydrogen atom, an alkali or alkaline earth metal cation, the residue of a nitrogen-containing C_3–C_9 heterocyclic compound, $[(Ph_3P)_2N]^+$, or the cation of a quaternary nitrogen-, phosphorus-, or arsenic-containing base, are used as catalysts of the carbonylation of methanol with formation of methyl acetate.[184] The process takes place in the presence of an iodine-containing promoting agent. The catalyst can also be formed *in situ* from cobalt and iron carbonyls in the presence of M^+. The method makes it possible to obtain acetaldehyde with a high degree of selectivity for the ratio $H_2:CO = 1:1$ at 140–200 °C. For the molar ratio $H_2:CO = 1.5$–3 and a temperature of 200–220 °C, ethanol is formed. The carbonylation of methanol in the presence of $Bu_4N.[FeCo_3(CO)_{12}]$ and CH_3I [molar ratio MeI/(Fe + CO) = 4], at a pressure of 270 atm of the 1:1 CO + H_2 mixture, and at a temperature of 180 °C leads to the formation of acetaldehyde and the aldehyde acetal in 62 and 18% yields respectively.[184]

The complexes $R_2Mg[Fe(CO)_{12}C_5H_5]_2$ and $R_4Mg[Co(CO)_3PBu_3]_2$ are effective carbonylation and hydroformylation catalysts, in the presence of which methanol is converted into methyl acetate in 37% yield (120 °C, 56 atm CO).[185]

In order to lower the alkyl halide concentration (to 0.3 M) and thus weaken the corrosive properties of the medium, it is recommended that the carbonylation of methanol to form acetic acid or methyl acetate be carried out with the addition of phosphonium salts of the type $(CH_3)(C_6H_5)_3P^+I^-$ to the system.[186]

Acetic acid is obtained in 88.2% yield by carbonylating methanol with carbon monoxide at a pressure of 10 atm and a temperature of 200 °C in the presence of the catalyst prepared from five parts (by weight) of graphite, one part of $RhCl_3$, and one part of $IrCl_3$.[187] Acetic acid is also formed from the 1:1 CO + H_2 mixture in the presence of cobalt and ruthenium carbonyls and amines, phosphines, arsines, stibines, bismuthines, and halogen-containing compounds used as promoting agents. Thus the interaction of CO with H_2 in an autoclave (280 atm, 220 °C) in the presence of $Ru_3(CO)_{12}$, $Co_2(CO)_8$, PPh_3, and $[CH_3(CH_2)_6]Ph_3P^+Br^-$ in an acid medium leads to the formation of a mixture of acetic acid, methyl acetate, ethyl acetate, and C_1–C_3 alcohols (74.5, 1.5, 15.5, and 8.5 wt.% respectively). In aprotic dipolar solvents (ethers, esters, polyesters, sulphones, or amides), mainly acetic acid with an admixture of propionic acid is formed from CO and H_2 in the presence of a soluble hafnium compound.[189]

Dicarboxylic acids are readily formed on carbonylation of lactones under mild conditions (40 atm CO, 180 °C):[190,191]



$n = 2$–4.

The carbonylation of γ-valerolactone in the presence of $RhCl_3.3H_2O$, CH_3I, and water in caproic acid afforded a mixture of 2-methylglutaric and adipic acids in 65.2 and 20.3% yields respectively.[190]

Dicarboxylic acids are formed with a high selectivity on carbonylation of glycols whose OH groups are not at neighbouring carbon atoms. Thus the interaction of butane-1,4-diol in acetic acid in the presence of $[Rh(PPh_3)(CO)Cl]_2$ and CH_3I (175 °C, 49 atm CO) results in the formation of adipic acid in 74.0% yield. An aromatic glycol (recorcinol) and *p*-phenylene diiodide gave rise to isphthalic and terephthalic acids in an overall yield of 15.0%.[192]

The Rh–Fe, Rh–Mn, Rh–Mn–Cl, Rh–Ru, and Rh–Cr bimetallic catalysts exhibit an appreciable activity in the synthesis of acetic acid from CO and H_2.[193] Acetic acid is also formed selectively in the carbonylation of methanol in the presence of the Rh–RM(Z).$[(O)_nR^1].(O)_mR^2$ complexes (where M = P, As, or Sb, Z = O, S, or Se, and R = H or alkyl; for $n = m = 0.1$, we have $R^1 = R^2 = OH$ and, when $n = m = 0$, MR^1R^2 represents a heterocycle), $RhCl_3$, CH_3I, and Ph_3PO.[194] The carbonylation of a mixture of methyl acetate and methanol, whose composition ranges from 1:1 to 3:1, with a mixture of CO and H_2 (from 1 to 40% H_2) in the liquid phase in the presence of rhodium compounds, alkyl iodides, phosphines, and also chromium or zirconium compounds results in the formation of acetic anhydride and acetic acid.[195] Under pressure (31.5 atm of CO, 1.5 atm of H_2, 180 °C) and in the presence of $RhCl_3.3H_2O$, CH_3I, $Bu_3P^+(Me).I^-$, and $Cr(CO)_6$, the above reaction takes place significantly less effectively.

Carboxylic acids having the general formula RCOOH (where R = C_1–C_{17} alkyl, Ph, or $PhCH_2$) are obtained by carbonylating the corresponding alcohols in the presence of a homogeneous catalyst containing molybdenum (or tungsten) compounds of an alkali metal as well as a promoting agent—inorganic or organic Br^- or I^- compounds.[196] The process can be carried out also under heterogeneous conditions on catalysts containing the above components (up to 10 wt.%) deposited on Al_2O_3, SiO_2, ZrO_2, clays, etc. In the carbonylation of methanol in acetic acid in the presence of NiI_2, $Mo(CO)_6$, LiI, and CH_3I (200 °C, 4.9 atm H_2, 37 atm CO), acetic acid is formed with a selectivity of 100%. The rate of its formation is 12.3 mol litre^{-1} h^{-1}.

Acetic and pripionic acids are formed jointly on γ-irradiation of methane mixed with CO and CO_2.[197,198] A mixture of acetic acid and methyl acetate is formed from methanol and a mixture of CO and H_2 (160 °C, 250 atm CO) in the presence of $Co_2(CO)_8$, NaI, and EtI.[199]

Ruthenium promoted with halogen-containing compounds is an effective catalyst of the carbonylation of alcohols. Thus the carbonylation of methanol in the presence of Ru/C and CH_3I affords a mixture of acetic acid and methyl acetate in 92.2 and 4.6% yields respectively.[200] The same products are obtained by carbonylating methanol with a mixture of CO and H_2 (80–98% CO) in the presence of a cobalt catalyst, a compound capable of generating I^-, and covalently bound iodine (1–30% of the amount of I^-).[201] Ammonium salts, alkali and alkaline earth metal salts, and phosphonium compounds are used as sources of I^-. Other promoting agents are X_2, HX, RX (where X = Cl, Br, or I), $CoBr_2$, CoI_2, CH_3I, I_2, HI, or $Co_2(CO)_8$. Thus a mixture of 10.5% of acetic acid and 80.5% of methyl acetate is formed in an overall yield of 91% from methanol and a mixture of CO and H_2 (95 and 5 atm respectively) at a pressure of 140 atm and a temperature of 160 °C in the presence of $Co_2(CO)_8$, NaI, and EtI.

Molybdenum deposited in an amount of 2.5 wt.% on activated carbon (gas carbon black) catalyses the carbonylation of methanol and dimethyl ether with formation of methyl acetate and the carbonylation of methyl acetate to form acetic anhydride.[101] Catalysts containing nickel on carbon, SiO_2, and Al_2O_3 as well as molybdenum on SiO_2 and Al_2O_3 are less active. Acetic anhydride is formed in 15% yield and a selectivity of 83% in the carbonylation of methyl acetate (250 °C, 46 atm CO) in the presence of 2.5 wt.% Mo/C and CH_3I.

Catalysts containing between 0.001 and 15 parts by weight of B_2O_3, P_2O_5 or $xB_2O_3.yP_2O_5$ (where $x = 0.05$–0.95 and $y = 0.05$ to 0.95), deposited on activated carbon, exhibit activity in the carbonylation of methanol with formation of methyl acetate.[203]

The study of the kinetics of the carbonylation of methanol[204] in acetic acid showed that the reaction is of first order with respect to methanol. In an aqueous medium, the order with respect to methanol is 0.75. The reaction mechanism involves the formation of CH_3I on interaction of CH_3OH with HI and its subsequent oxidative addition to the complex $[Rh(CO)_2I_2]^-$. This results in the appearance of the complex $[CH_3Rh(CO)_2I_3]^-$, subsequently converted into $[(CH_3CO)Rh(CO)_2I_3]^-$, which decomposes into CH_3COI and $[Rh(CO)_2I_2]^-$. The effectiveness of the solvents is determined by the solubility of CH_3I in them. Thus, an increase in the concentration of methanol in water increases the solubility of CH_3I, which leads to an increase in the rate of carbonylation. In acetic acid, an increase in the concentration of methanol does not affect the solubility of CH_3I.[204]

Acetaldehyde is formed in the vapour-phase carbonylation of methanol in the presence of CH_3I and the Co/C catalyst promoted with palladium salts and alkali metals (after their reduction). The process is carried out in a flow apparatus (180–240 °C, 10–65 atm, $CO/H_2 = 1$). The promoting effect of palladium salts and alkali metals is associated with the intensification of the hydrogenating function of the cobalt catalysts.[205]

Modification of the nickel catalysts with palladium or copper chlorides or nitrates increases the effectiveness of the synthesis of acetic acid and methyl acetate via the vapour-phase carbonylation of methanol. Cl_2, Br_2, or I_2 or their volatile compounds are used as

promoting agents in an amount of 0.05–0.4 of a mole per mole of methanol. The vapour-phase carbonylation of methanol (300 °C, 1 atm, a mixture of CO and CH_3I in molar proportions of 30.1 : 8.6 : 1) in the presence of a catalyst containing 8.7% Ni and 0.03% Pd on activated carbon produces a mixture of acetic acid and methyl acetate in an overall yield of 80%. The degree of conversion of methanol is 65% and the productivity reaches 0.3 kg (AcOH + AcOMe) (litre cat.)$^{-1}$ h^{-1}. The catalysts retain their stability for two weeks of continuous operation.[206] Methanol can be converted into methyl acetate on a palladium catalyst (0.1–1% Pd) deposited on a dealuminated and decationated mordenite in a flow system. The degree of conversion of methanol at 250 °C, a pressure of 1 atm, and a space velocity of 0.4 h^{-1} in the presence of added 10% CH_3I in methanol is 49.1%.[207]

Methanol can be carbonylated to acetic acid and methyl acetate in the presence of effective homogeneous systems containing Group VIII metal compounds. The compounds RX (where R = H or C_1–C_3 alkyls and X = Cl, Br, or I) as well as Group IA and IIA metals, transition metal iodides (or carboxylates), and nitrogen-containing bases are used as promoting agents. Such a reaction takes place, for example, in an autoclave in the presence of $Pd(OAc)_2$, 2,2′-bipyridyl, MeOAc, H_2O, MeI, and NaI (178 °C, 1110 atm), a mixture of acetic acid and methyl acetate being formed at a rate of 0.14 kg litre^{-1} h^{-1}.[208]

Heterogeneous rhodium catalysts on carriers, including faujasites, exhibit a higher activity when they are obtained from $RhCl_3$ than the catalysts obtained from the complex $[Rh(NH_3)_5Cl]Cl_2$. In more active catalysts, the metal is distributed on the surface of the carrier more uniformly and the rhodium particle size is about 9 Å.[209]

Among the catalysts based on Ni, Co, and Fe which have been investigated,[210] the highest activity in the carbonylation of methanol was shown by nickel catalysts on activated carbon. The use of other carriers (γ-Al_2O_3, SiO_2, carbon blacks, and graphite) yielded worse results. In the presence of the iron and cobalt catalysts on activated carbon, the main carbonylation product was dimethyl ether and the yield of acetic acid and methyl acetate did not exceed 11%. At 300 °C, a pressure of 11 atm, and for the molar ratios CO : MeOH : MeI = 20 : 19 : 1, acetic acid and methyl acetate were obtained from methanol in 69.1 and 21.6% yields respectively in the presence of 2.5% Ni/C. The degree of conversion of methanol was 69.1%. The primary reaction products are Me_2O and AcOMe, acetic acid being formed on their subsequent carbonylation.

The selective synthesis of methyl acetate is carried out by the liquid-phase carbonylation of methanol in the presence of the Ru–Co - onium salt (0.25 : 1 : 10–50) catalyst in 1,4- or 1,3-dioxans. The interaction of methanol with CO in the presence of $Rh(OH)_4$, $Co_2(CO)_8$, and Bu_4PBr^- in 1,4-dioxan (180 °C, 245 atm) affords methyl acetate in 83% yield. Ethyl acetate is formed as a side product in 9% yield. The degree of conversion of methanol reaches 95%.[211]

The selective synthesis of methyl acetate from methanol also takes place in the presence of Group VIII metal compounds mixed with pentachlorobenzenethiol or its salts. Thus the carbonylation of methanol in the presence of the $RhCl_3$–C_6Cl_5SH system (175 °C, 50 atm CO) gives rise preferentially to the formation of methyl acetate.[212] When nickel compounds, a phosphine promoting agent, and methyl iodide are used, a mixture of acetic acid and methyl acetate is obtained from methanol. For example, the carbonylation of methanol in the presence of NiI_2, PPh_3, and MeI (28 atm, 150 °C) makes it possible to obtain a mixture of acetic acid and methyl acetate in 73.0 and 25.3% yields respectively.[213]

The selectivity in the formation of methyl acetate in the vapour-phase carbonylation of methanol on the Rh/NaX catalyst falls when the concentration of the rhodium introduced by the method involving the ion exchange of the $[Rh(NH_3)_5Cl]^{2+}$ cations, increases from 0.4 to 4%.[214] The reaction selectivity also falls (approximately by a factor of 4) if the rhodium catalyst is subjected to a preliminary heat treatment in air at 200 °C but remains unchanged if the heat treatment is performed at a higher temperature, up to 422 °C. Heat treatment in H_2 or CO at 320–350 °C deactivates the catalyst to a lesser extent than heat treatment in air. The treatment in CO does not affect the yield of dimethyl ether, while the treatment in H_2 increases it by approximately a factor of 1.5 compared with the heat treatment in air.

Catalysts for the homogeneous carbonylation of methanol having the general formula $R_pM[M'(CO)_mL_n]_2$ (where R is a nitrogen-containing base capable of being coordinated to Group IIA metals, M is a Group IIA metal, M′ is a Group VIB, VIIB, or VIII transition metal, L is a polyfunctional ligand capable of being coordinted to the transition metal, p = 1–4, m = 1–5, n = 0–4, and n + m = 5) have been prepared. The carbonylation of methanol in the presence of $(THF)_4.Mg[Co(CO)_3PBu_3]_2$ and CH_3I in benzene (120 °C, 56 atm CO) affords methyl acetate in 37% yield. Dimethyl ether is hardly formed.[215]

The carbonylation of dimethyl ether with formation of methyl acetate is carried out in the presence of palladium compounds, an iodine-containing promoting agent, and a tertiary amide or alkali or alkaline earth metal salts of a carboxylic acid.[216] The process, which is performed at a CO partial pressure of 30–150 atm and 180–220 °C, is distinguished by high selectivity.

The kinetics of the carbonylation of isopropyl alcohol with formation of isobutyric or n-butyric acid in the presence of the $RhCl_3$–HI catalytic system have been investigated.[217] The rate of carbonylation at 170 °C in an acetic acid–water mixture falls with increase in pressure. The reaction is of first order with respect to Rh, while the order with respect to HI is less than unity. Only the anionic species $[Rh(CO)_2I_2]^-$ have been detected spectroscopically. With increase in pressure from 14.6 to 205 atm, the isobutyric acid/n-butyric acid ratio increases from 0.7 to 1.6. The ratio is independent of the concentrations [Rh] and [HI]. The addition of propene to the mixture tends to increase the content of the n-isomer while the addition of an iodide slightly accelerates the reaction but does not affect the isobutyric acid/n-butyric acid ratio.

On treatment with the synthesis gas in the presence of a rhodium compound, a Group II metal iodide, and a Group VIII metal iodide (or bromide), ethers and esters are converted into mixtures of carboxylic acids or their esters, in which the alkyl group contains one CH_2 group more. Thus the interaction of methyl acetate with the synthesis gas in the presence of $RhCl_3$, $RuCl_3$, and ZnI_2 in 15-crown-5-(or 18-crown-6-) ethers results in the formation of ethyl acetate and acetic acid among other products.[218]

The reductive carbonylation of methanol in the presence of salts containing the anion $[FeCo_3(CO)_{12}]^-$ at 220 °C leads to the formation of ethanol in 73% yield. The reaction proceeds via stages involving the formation of acetaldehyde and methyl acetate. Under optimum conditions, the yield of acetaldehyde reaches 80–82%.[219]

Active nickel catalysts have been proposed for the synthesis of acetic acid by the isomerisation of methyl formate in the presence of iodine-containing promoting agents as well as compounds having the formula VR^1R^2, where V = N, P, Sb, As, or Bi and R, R^1, and R^2 = H, C_1–C_{10} alkyl, cycloalkyl, or aryl.[220] The reaction is carried out at 170–190 °C at normal or elevated pressures.

An effective method has been developed for the synthesis of esters from polyhydric alcohols, hex-1-ene and carbon monoxide in the presence of a cobalt catalyst and γ-picoline as the promoting agent. The catalyst is prepared from cobalt octanoate, γ-picoline, H_2O and CO in a separate apparatus (170 °C, 200 atm). The synthesis is carried out in apparatus of the bubbler type and the CO can contain up to 5 vol.% H_2. The esters obtained, for example, pentaerythritol tetraheptanoate, are used as components of a lubricating oil, plasticisers, and surfactants.[221-224] The initial polyhydric alcohols may be di- and tri-pentaerythritols, pentaerythritol, tris- or tetrakis-(hydroxymethyl)propanes, etc. and the olefins may be, apart from hex-1-ene, also but-1-ene, pent-1-ene, dec-1-ene, dodec-1-ene, etc. A method has been developed for the purification of the final product involving the removal of the cobalt impurities by treatment with aqueous solutions of alkali or alkaline earth metal oxides, carbonates, or bicarbonates at 120–140 °C.[221]

In the synthesis of aliphatic esters from alcohols and CO on an industrial scale, it is essential to use lower temperatures and pressures than is provided for in the majority of the patented processes. By carrying out the process in the presence of traces of H_2 and by using a complex of pyridine with cobalt carbonyl in proportions of 2:1 as the catalyst, it is possible to reduce the reaction temperature from 160–180 °C to 80–100 °C and the pressure from 150–200 to 20 atm.[225]

It has been established[226] that, in order to obtain active and stable deposited rhodium catalysts, the carriers must have definite acid–base properties. The use of oxide carriers with pronounced acid–base properties, such as Al_2O_3 or Al_2O_3–SiO_2, promotes the formation of rhodium complexes of the anionic type $[O \rightarrow Rh(CO)_2Cl]^-$ on the surface. When neutral carriers (SiO_2) are used, rhodium complexes of the type $O \rightarrow Rh(CO)_2Cl$, which are inactive in catalysis, are formed.

A catalyst for the carbonylation of methanol, exhibiting an activity higher by a factor of 50–100 than the usual rhodium catalysts, has been obtained by ion exchange between the NaX zeolite and $[Rh(NH_3)_5Cl]Cl_2$ and subsequent heating to 400 °C in a stream of N_2.[227] It works effectively at temperatures in the range 130–150 °C.

The chlororhodium-phthalocyanine catalyst for the carbonylation of methanol, used together with CH_3I and the sulphonic acids $CH_3C_6H_4SO_3H$, CH_3SO_3H, $PhCH_2SO_3H$, etc., is prepared by treating phthalocyanine or its carboxysulpho-derivatives with rhodium, cobalt, and iridium halides and also phosphorus-, sulphur-, arsenic-, or nitrogen-containing anions.[228] Before use, the catalyst is activated in an atmosphere of CO and H_2 at temperatures in the range 50–100 °C. The carbonylation of methanol in an autoclave (200 °C, 80 atm CO, 80 atm H_2) in the presence of a complex prepared from sodium phthalocyaninetetrasulphonate and $RhCl_3$ afforded a mixture of methyl acetate and acetic acid in 11 and 9% yields respectively.

The addition of lanthanide oxides to the nickel or cobalt catalysts makes it possible to carbonylate methanol with formation of acetic acid and methyl acetate without using halogen-containing promoting agents. The products are formed in high yields at temperatures in the range 130–200 °C and CO pressures from 1 to 50 atm.[229] The catalyst is first reduced in a stream of H_2 at 300–400 °C for 1 h and is then treated with CO (10–80 vol.%) containing N_2, CH_4, or C_2H_6 at 250–300 °C for 1–3 h. A mixture of methyl acetate, acetic acid, and methyl formate has been obtained in yields of 87.0, 8.7, and 0.87% respectively from methanol and carbon monoxide (in proportions by volume of 1:9) at 190 °C and a pressure of 5 atm on a catalyst containing 0.5% Rh and 15% of lanthanum oxide on SiO_2. Catalysts containing platinum (0.8–2.0 wt.%), cerium (15–20%), or lanthanum (10–20%) deposited on Al_2O_3 and TiO_2 are also active in this reaction.[230]

The rhodium ions in the Rh/NaX catalyst obtained by ion exchange are in a state close to their state in a homogeneous catalyst, but the activation energy for the heterogeneous carbonylation of methanol is nevertheless twice as high as for the homogeneous carbonylation.[231] The Rh/NaX catalysts are stable only at temperatures not exceeding 220 °C. The reaction is of zero order with respect to rhodium.

Oxidative carbonylation of fluorinated alcohols with carbon monoxide in the presence of Group IIB elements in the ionic form can result in the formation of the corresponding carbonates. Fluorine-containing carbonates and polycarbonates based on them have found extensive application in the pressing and moulding of plastics. The reaction takes place under mild conditions. Thus the interaction of CF_3CH_2OH with CO bubbling through it at atmospheric pressure and 20 °C in the presence of $Hg(OAc)_2$, 1,2,2,6,6-pentamethylpiperidine, and the sodium salt of dimethyl sulphoxide afforded $(CF_3CH_2O)_2O$ in 90% yield.[232]

But-3-enoic acid is obtained by the liquid-phase carbonylation of allyl alcohol in the presence of the palladium complex $LnPdCl_2$ (where L = nitrile, phosphine, or amine and n = 0 or 2) at 75 to 200 °C and a pressure of 35–140 atm.[233] Thus the carbonylation of allyl alcohol in acetic acid ($PdCl_2$, 80 °C, 90 atm CO) produces but-3-enoic acid in 64% yield. In acetonitrile, the yield falls to 40%. But-3-enoic acid is a valuable intermediate in the synthesis of γ-butyrolactone and 2-pyrrolidinone.

Nickel and cobalt catalysts promoted with compounds of Group IV elements (Si, Ge, and Sn), Group IA and IIA elements (Li, Ca, and Sr), as well as nitrogen-containing bases showed a high effectiveness in the synthesis of acetic acid from methanol. The promoting agents are iodine-containing compounds and aluminium, zinc, copper, lanthanum, and cerium iodides or bromides. Thus the carbonylation of methanol in acetic acid in the presence of nickel powder, SnI_4, 2,4-dimethylpyridine, CH_3I, and LiOAc (195 °C, 20 atm CO, and 3 atm H_2) gave rise to acetic acid in 97.6% yield.[234] The use of compounds (cobalt and nickel) with added alkyl- or arylphosphines and iodine-containing promoting agents as catalysts makes it possible to carry out the liquid-phase carbonylation of methanol. Thus the carbonylation of methanol (350 atm CO, 200 °C) in the presence of $Co(AcO)_2.4H_2O$, HI, and Bu_3P in an aqueous medium results in the formation of a mixture of methyl acetate and acetic acid in an overall yield of 91.0%.[235] Methyl acetate is formed selectively in the carbonylation of methanol (125 atm, 120 °C) in the presence of $Mn_2(CO)_{10}$ and CH_3I.[236]

The treatment of esters of mono- or di-carboxylic acids with the synthesis gas in the presence of homogeneous cobalt and rhodium compounds as well as LiI or LiBr results in the formation of aldehydes, carboxylic acids and their esters. Thus the interaction of methyl acetate with the synthesis gas (CO/H_2 = 1, 180 °C, 210 atm) in the presence of $Co(AcO)_2.4H_2O$, $Rh(acac)(CO)_2$, and LiI produced a mixture of MeCHO, HOAc, and AcOEt, the selectivity in the formation of acetaldehyde amounting to 86%.[237]

Lower carboxylic acids are obtained by the carbonylation of alcohols in the presence of nickel complexes and iodine-containing promoting agents. Acetic acid has been formed in a high yield in the interaction of methanol with CO (150 °C, 21 atm CO) in the presence of $(Ph_3P)_2Ni(CO)_2$, PPh_3, and CH_3I.[239] In order to reduce the corrosion of the apparatus by iodine-containing compounds, it is

recommended that alcohols be carbonylated with formation of acids and their esters in solution in aryl acetates.[240]

A method has been developed for the transesterification and carbonylation of the esters of lower aliphatic C_1–C_5 carboxylic acids and C_1–C_4 alcohols by carbon monoxide and phenols in the presence of Group VIII metal compounds with added iodine compounds as promoting agents.[241] The reaction is accelerated by tertiary amines NRR^1R_2 or the compounds $N(COR)R^1R^2$, where R, R^1, and R^2 = H, alkyl, or aryl. Thus the interaction of methyl acetate with CO and phenol (30 atm CO, 180 °C) in acetic acid in the presence of $RhCl_3$ and CH_3I converted half of the initial methyl acetate into acetic acid and phenyl acetate (the degrees of conversion were 97.5 and 96.8% respectively).

The $RhCl_3$–graphite and $RhCl_3$–graphite–I_2 systems, prepared by depositing $RhCl_3$ and I_2 on petroleum or coal coke in a high vacuum or in an inert gas atmosphere at 300 °C, are effective catalysts of the carbonylation of methanol to acetic acid.[242] Thus, by passing an MeOH : CO = 1 : 4 mixture at a space velocity of 45 cm^3 min^{-1} through a glass tube charged with the catalyst (2% $RhCl_3$ + 0.4% I_2)/C (with a specific surface of 10 m^2 g^{-1}) at 200 °C, methyl acetate and acetic acid have been obtained in 35.5 and 8.5% yields.

Carboxylic acids and esters are obtained together on interaction of compounds having the general formula RCO_2R' with the synthesis gas:

$$RCO_2R' + CO + H_2 \begin{cases} \longrightarrow RCOOH + R'COOH, \\ \longrightarrow RCH_2COOR', \\ \longrightarrow R'COOR. \end{cases}$$

The reaction is catalysed by rhodium compounds as well as compounds of other Group VIII metals, phosphines, and alkyl iodides or bromides. Thus treatment of methyl acetate with a 1 : 1 mixture of CO and H_2 in the presence of $RuCl_3$, $RhCl_3$, MeI, and PPh_3 (160 °C) leads to the formation of a mixture of acetic acid and ethyl acetate.[243]

Carboxylic acids and their anhydrides are obtained by carbonylating ethers or esters in the presence of metals or Group VIII metal compounds, Br^-, I^-, or their compounds. Thus a mixture of acetic acid and acetic anhydride can be obtained in a high yield by treating methyl acetate with carbon monoxide in the presence of the rhodium acetate dimer, 1-methylimidazole, and CH_3I at 175 °C.[244]

The interaction of carboxylic acids with the synthesis gas in the presence of rhenium and ruthenium compounds leads to the formation of acid esters. Thus treatment of acetic acid with a 1 : 1 mixture of CO and H_2 in the presence of $Ru_3(CO)_{12}$ and $NaRe(CO)_2$ (240 °C, 245 atm) affords a mixture of methyl and ethyl acetates.[245]

A method has been proposed for the preparation of methyl formate by carbonylating methanol in the presence of sodium methoxide. The introduction of $H_2N(CH_2)_6NH_2$ into the reaction zone increases the degree of conversion of methanol, while the addition of water poisons the catalysts.[246–249] The formation of methyl formate is facilitated in the presence of 0.1–30 wt.% of pyridine and 0.1–28 wt.% of the hydroxylated epoxide oligomer $HO(CH_2CHRO)_nH$ (where n = 2–600 and R = H or Me).[247] The reaction is carried out in the temperature range 60–100 °C. Conditions have been found for the hydrolysis of methyl formate with formation of formic acid in the presence of a strongly acid sulphonic acid cation exchanger based on styrene and divinylbenzene.[248,249] The hydrolysis is carried out at 60–100 °C and the resulting reaction mixture is transferred to a second vat-reactor where the hydrolysis is completed at 100–105 °C.

The interaction of methanol with the synthesis gas (CO/H_2 = 1) in the presence of $Al(acac)_3$ (250 °C, 200 atm) results in the formation of methyl acetate and methyl formate with selectivities of 62.5 and 35.1% respectively. The degree of conversion of methanol is 21%.[250]

Treatment of C_1–C_{20} alkyl, aryl, arylalkyl, and alkylaryl formates with the synthesis gas in the presence of a catalytic system containing rhodium compounds and LiI leads to the formation of the corresponding carboxylic acids. Thus the interaction of methyl formate with a 1 : 1 mixture of CO and H_2 in the presence of the $Rh(CO)_2(acac)_2$–LiI system results in the formation of acetic acid with a selectivity of 95% for a formate conversion of 65%.[251]

The technology of the synthesis of formic acid via methyl formate has been investigated on a scaled-up experimental apparatus. A procedure for the isolation of pure formic acid after the stage involving the hydrolysis of methyl formate and its concentration to 96% has been developed.[252]

The carbonylation of alcohols with formation of branched carboxylic acids proceeds under mild conditions on effective acid catalytic systems.[253–256] Thus trimethylacetic acid has been obtained with a high selectivity in the interaction of isobutyl alcohol with carbon monoxide (7.5 atm) in a liquid-phase reactor with vigorous stirring (1000 rev min^{-1}) at 60 °C in the presence of the $HF : BF_3 : H_2O$ = 5.1 : 1 : 1 catalytic system.[253]

The esters of αα-branched carboxylic acids are obtained in the presence of BF_3 with added copper(I), silver(I), or gold(I) carbonyls, formed in a strongly acid medium under mild conditions (temperature from −20° to +20 °C, 1 atm).[254]

Trimethylacetic acid is obtained selectively by carbonylating isobutyl alcohol in the presence of H_2SO_4 as the catalyst and ethyl formate as the carbonylating agent.[256] The reaction takes place at atmospheric pressure, 40–60 °C, and with molar ratios H_2SO_4 : 1-hexanol : $HCOOC_2H_5$ = 8–10 : 1 : 4. The mild process conditions are due to the formation of activated carbon monoxide on decomposition of ethyl formate in an acid medium and the evolution of ethanol as the esterifying agent.

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In conclusion, we shall identify certain problems associated with the catalytic syntheses based on carbon monoxide. Despite the promising nature of many methods and the availability of large resources of carbon monoxode derivatives, there are as yet few industrial processes using this gas. The main causes of this situation are as follows: (1) the complexity and high cost of the majority of catalytic systems known at present; (2) the necessity to used special apparatus resistant to the corrosive action of the catalytic systems; (3) the insufficient number of highly selective and very stable catalysts which can be readily removed from the reaction products.

The introduction into industrial practice in recent years of the synthesis of acetic acid by the carbonylation of methanol can be regarded as one of the greatest advances in the field of carbonylation. Despite major successes achieved in their theoretical study, other processes have not so far found much practical application. Analysis of the extensive literature data presented in the present review shows that in most cases the proposed catalytic systems,

ensuring a high selectivity, are extremely complex and are frequently insufficiently stable. The questions of the repeated use of such systems have not been resolved.

Since virtually all carbonylation processes take place only at elevated pressures, a far-reaching study of their mechanism is difficult. Therefore in most cases the role of each component of the catalytic system is not entirely clear and so far the catalysts are selected empirically.

The present review naturally cannot embrace the entire literature devoted to the catalytic syntheses based on carbon monoxide. It includes only the main studies demonstrating the principal trends in the development of this important branch of science and technology.

The concentration of the research effort on the most promising and most thoroughly developed aspects of the field will apparently permit in the immediate future a significant expansion of the range of processes based on the use of carbon monoxide.

One should note that, among all types of the catalysts of the carbonylation reactions which have been investigated, the homogeneous catalysts exhibit the highest activity and selectivity. However, their separation from the reaction mixture presents certain difficulties. One way of solving this problem is the development of a method for the immobilisation of the soluble catalyst on an insoluble carrier. Such hybrid catalysts, which combine the high activity and selectivity of homogeneous systems with the ease of separation characteristic of heterogeneous catalysts, will probably find extensive application in industry. Another possible solution of the problem of the catalyst involves the carrying out of the reaction in a two-phase liquid–liquid system in which the catalyst and reaction products are dissolved in different phases.

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