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Recent advances in the methanol carbonylation reaction into acetic acid

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*Dedicated to Professor Armando J.L. Pombeiro for his outstanding achievements in Coordination
Chemistry and Catalysis.*

Abstract. Although the high efficiency of the homogeneous processes, using rhodium or iridium complexes, was clearly demonstrated industrially, heterogeneous catalysts offer the advantages of facile product separation and vapor phase operation, which often limit catalyst losses. Both noble and non-noble metal homogeneous and heterogeneous catalyzed carbonylation of methanol have been studied for many years. In this short chapter, we intend to analyze the recent evolutions of the most promising catalytic systems for this important reaction of catalysis. A presentation by metals was chosen, always referring to the origins of the first catalytic systems.

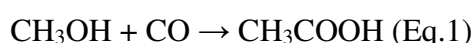
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1. Introduction and history of the methanol carbonylation reaction

Today, acetic acid (ethanoic acid) is at 85 % produced by methanol carbonylation. Its production is significantly growing since 2015, with 13 million tons to reach 18 million tons in 2020, with thus an approximately 5 % annual growth.¹ Methanol, whose production was 85 million tons in 2016, is one of the first building blocks in a wide variety of synthetic products, and is also used as a fuel additive.² The main use of acetic acid is related to its transformation in vinyl acetate monomer, ethyl-, propyl-, n-butyl- and isobutyl-acetate, acetic anhydride, and as solvent in the synthesis of terephthalic acid.³ Acetic acid is the second aliphatic compound, after methanol, which originates from the CO/H₂ chemistry. As syngas can be generated from various sources, methanol constitutes an abundant and low cost precursor in the synthesis of acetic acid, provided the carbonylation process (Eq.1) is highly selective, and the recycling of the catalyst as well as the purification steps are efficient.



Intense research has been performed after the discovery in 1913 that acetic acid could be synthesized from methanol and carbon monoxide.^{4,5,6,7} Indeed, from a mixture containing 62 % CO and 28 % H₂ operating at pressures over 100 bar and temperatures of 300-400 °C with the presence of catalysts containing either cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, or zinc, large quantities of hydrocarbons are produced, but also alcohols, aldehydes and ketones as well as acetic acid and its homologues. The two examples detailed in the two first patents are related to cobalt or osmium and zinc on various supports.^{4,5} Later, Reppe and his research group in I.G. Farben, and then BASF, patented the catalytic activity of iron, cobalt and nickel in the presence of an iodide copper salt to carbonylate methanol to acetic acid and methylacetate, most examples being focused on nickel at 230-340°C and 180-200 bar.⁸ BASF and later British Celanese developed intense work, claiming the use of mainly iron with low activity, and cobalt as well as nickel carbonyls in the presence of iodine or iodide salts, for performing the carbonylation reaction at high pressures and temperatures.⁹ The corrosion issues encountered when using iodide promoters, leading to the presence of corrosion metals into the reaction medium with consequent poisoning of the catalytic system, were only solved at the end of the 1950s when the highly resistant Hastelloy[®] Mo-Ni alloys were developed.¹⁰

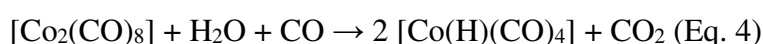
Nickel powder was claimed to convert 89.1 % of methanol at 295 °C, 200 bar for 1 day in the presence of the CuI₂ promoter into acetic acid (64.5%) and methyl acetate (24.6%).⁸ This yield is significantly higher than the one obtained with [Fe(CO)₅]/CuI₂ at 300 °C, 200 bar for 36 h (30 % and 2 3%, respectively). Nickel carbonyl, [Ni(CO)₄], is preferred with 37% yield/hour obtained into a tubular reactor.^{11,12} When NiI₂ and I₂ are simultaneously deposited on activated carbon (AC) support, methyl acetate can be produced by a continuous process in a single passage at 30 bar of CO/H₂/H₂O, 195-215 °C with a 50.5% conversion.¹³ However, in the process there is some loss of catalytic active species from the reaction zone to the gaseous

effluent so that it is necessary to introduce continuously NiI₂ and I₂.¹⁴ Many efforts have been devoted to improve the performances of the catalyst and the most significant reports can be quoted. Introduction into the reactor of nickel bromides or iodides containing ammonium or phosphonium halides to provide [NR₃R']₂[NiI₄] or [PR₃R']₂[NiI₄] or the pyridinium or pyrrolidinium Ni(II) complexes results in the facile recycling of the catalyst, even if small amounts of [Ni(CO)₄] are still produced at 190 °C and 700 bar.¹⁵

Although the Co powder/CuI system gave more modest yields (16 % acetic acid and 54 % methyl acetate)¹² than nickel, BASF focused his attention on the development of the cobalt process, presumably because highly toxic [Ni(CO)₄] is too volatile and difficult to manage.³ Under harsh operating conditions (250 °C and 680 bar),⁸ the selectivity to acetic acid is 90% based on methanol, and 70 % based on CO, mainly due to the Water-gas shift (WGS) reaction (Eq.2).¹²



The CoI₂ salt reacts with carbon monoxide to produce the dicobalt octacarbonyl [Co₂(CO)₈] precursor, and then the hydrido cobalt tetracarbonyl [Co(H)(CO)₄] resting state (Eq.3 and 4).⁷



This cobalt-catalyzed methanol carbonylation has been industrialized by BASF in 1960 and commercialized in 1963. Twenty years later, two acetic acid plants were operating in Germany with a capacity of 50 000 T.y⁻¹, and in the USA (Louisiana, Borden Co plant, 65 000 T.y⁻¹) before to abandon this process due to the high pressure conditions and the mediocre selectivity by comparison with the rhodium Monsanto process.¹⁰

In 1968, Paulik and Roth unveiled the capacity of rhodium precursors, such as RhCl₃·3H₂O, [RhCl(CO)(PPh₃)₂], or [Rh₂(μ-Cl)₂(CO)₄], in the presence of halogen promoters,

to carbonylate methanol into acetic acid at 175°C and 28 bar.^{16,17} This rhodium system complemented a first patent devoted to iridium, platinum, palladium, osmium and ruthenium catalysts.¹⁸ The selectivity for rhodium is higher than 99 % and the turnover numbers can reach 10⁵ in a continuous process.¹⁷ In 1970, the first industrial plant went on stream in Texas City with a capacity of 150 000 T.y⁻¹ of acetic acid.¹⁰ Seminal mechanistic studies have been performed by the Monsanto researchers,^{19,20} particularly by Forster.^{21,22,23,24} From the numerous studies carried on the mechanism and the kinetics of the reaction, especially by Maitlis and Haynes *et al.*, the more recent reviews allow to summarize the main points of the mechanisms.^{3,25,26,27} The active species is the anionic complex [RhI₂(CO)₂]⁻ (Fig. 1a²⁸), on which the rate determining step is the oxidative addition of CH₃I. In the process conditions the simultaneous presence of methanol and acetic acid leads to significant quantities of methyl acetate, which is transformed into CH₃I and acetic acid in the presence of HI (Eq.5).



As the [RhI₂(CO)₂]⁻ complex catalyzes also the water-gas shift reaction (Eq.2), the selectivity based on CO is 90% and large amounts of CO₂ are co-produced, since for maintaining the stability of the catalyst, it is necessary to have at least 14% water in the medium. At this high water content, the overall rate is first order in both the rhodium complex and **methyl iodide**, and zero order in both methanol and CO reactants. The activation parameters, determined by Dekleva and Forster,²⁹ are $\Delta H^\ddagger = 63.6 \text{ kJ.mol}^{-1}$ and $\Delta S^\ddagger = -116 \text{ J.mol}^{-1}.\text{K}^{-1}$. This large negative entropy of activation is consistent with the nucleophilic attack of the rhodium center on the carbon atom of CH₃I to form the [RhI₂(CH₃)(CO)₂] neutral intermediate, which further coordinates the I⁻ ligand as in a classical S_N2-type oxidative addition. This short-lived [RhI₃(CH₃)(CO)₂]⁻ complex was identified by Maitlis and Haynes, and presents a *fac,cis* geometry.^{30,31} Subsequent rapid migratory CO insertion occurs in the Rh-CH₃ bond to provide in coordinating solvents the [RhI₃(COCH₃)(CO)(solv)]⁻ species, which coordinates CO to give

the thermodynamically preferred *mer,trans*-[RhI₃(COCH₃)(CO)₂]⁻ complex, as shown by its X-ray crystal structure with the bis(triphenylphosphoranylidene)ammonium counter-cation.³² This complex was also isolated from the oxidative addition of CH₃COI to [RhI₂(CO)₂]⁻.³³ Finally, reductive elimination of CH₃COI occurs, scavenged by water to generate acetic acid, HI and [RhI₂(CO)₂]⁻ for a new catalytic cycle. The high water concentration to avoid the accumulation of inactive [RhI₄(CO)₂]⁻ and the precipitation of RhI₃ leads to a costly separation process to dry acetic acid in one of the three distillation columns of the plant.^{26,27}

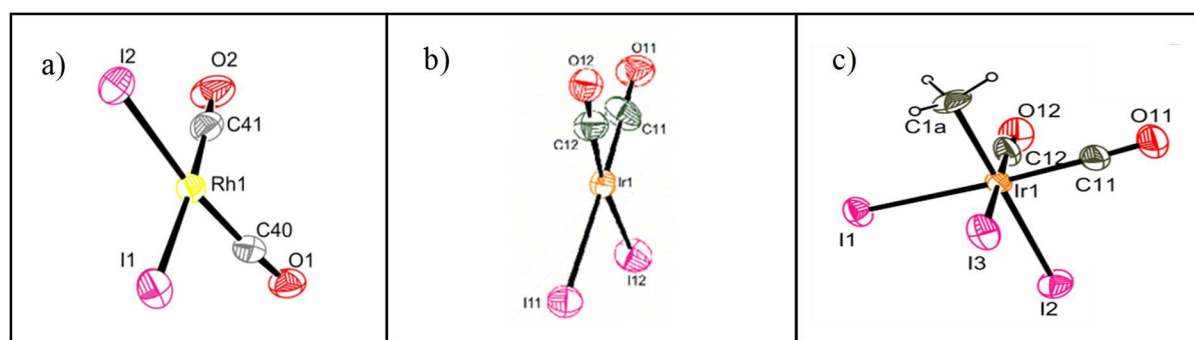
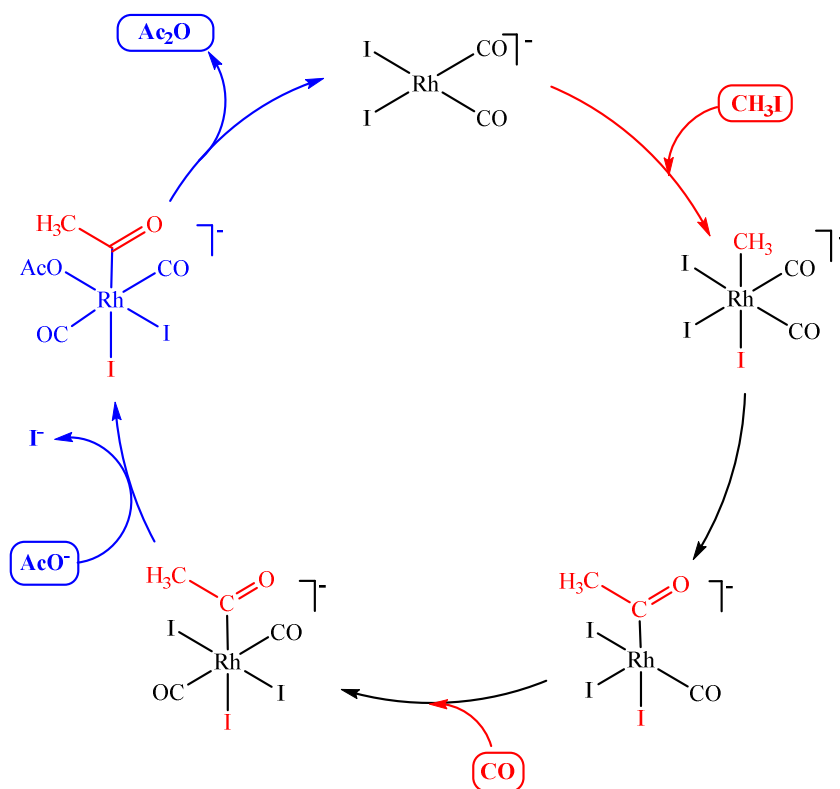


Figure 1. X-ray crystal structures of the anionic part of the [PPN][RhI₂(CO)₂], [PPN][IrI₂(CO)₂] and *fac,cis*-[PPN][IrI₃(CH₃)(CO)₂] complexes (adapted from ref.²⁸, the PPN⁺ group being omitted).

In the low-water content process, discovered by Hoechst Celanese,³⁴ the catalyst stability and reactor productivity are obtained by addition of LiI to the rhodium catalyst. This Acid Optimization (AO[®]) technology using thus Li[RhI₂(CO)₂] (the Li₂[RhI₃(CO)₂] intermediate has even been considered) leads to enhanced carbonylation rates, increasing CH₃OH and CO efficiencies, and results in extended capacities of the plants.³ Below 5% water content, the rate-determining step becomes the reductive elimination reaction of acetyl iodide.³² This change in the relative reaction rates in the catalytic cycle must be related to the

observations of Cole-Hamilton, Haynes and coworkers. **Indeed**, when using the highly σ -donating $C_5Me_4(CH_2)_2PEt_2$ ligand, the rhodium center of $[(\eta^5-C_5Me_4(CH_2)_2PEt_2)RhI(COCH_3)]$ is so electron rich that the reductive elimination becomes the rate-determining step, **and** accumulation of the acetyl complex occurs in the medium.³⁵ Another pathway for Rh-catalyzed methanol carbonylation at low water content characterized by a low energy profile has been identified (Scheme 1), in which an iodo ligand is substituted by an acetate ion in $[RhI_3(COCH_3)(CO)_2]^-$ to give $[RhI_2(COCH_3)(COOCH_3)(CO)_2]^-$.³²



Scheme 1. Catalytic cycle of $[RhI_2(CO)_2]^-$ at low water contents producing acetic anhydride
(adapted from ref.^{28,32}).

The reductive elimination of acetic anhydride occurs very easily since it liberates 36 kcal.mol⁻¹, **as calculated by DFT**, and regenerates $[RhI_2(CO)_2]^-$.²⁸ Acetic anhydride reacts then

with water to give acetic acid. In the less abundant water carbonylation process, the separation of acetic acid from water is easier at the distillation stage, the catalyst is less prone to precipitation, and the CO efficiency is largely improved with regard to the Monsanto process, due to reduced amounts of the WGS reaction.

To facilitate the separation of the catalyst from the reactants and products, many attempts have been made to graft the $[\text{RhI}_2(\text{CO})_2]^-$ rhodium complex onto solid supports. A polyvinylpyridine resin, able to support high temperatures, has been developed by Chiyoda and UOP.^{36,37,38} Under the carbonylation conditions, the pyridine nitrogen atom is quaternized by CH_3I and stabilizes the anionic Rh species. In this AceticaTM process, the rhodium catalyst on the polyvinylpyridine resin support remains confined in the reactor and not lost downstream, unlike processes in which the reduced pressures generally induce vaporization loss of metal carbonyl complexes.^{39,40} The resin allows to perform the methanol carbonylation at 160-200°C and 30-60 bar, and at low water content (3-7%) so that the formation of CO_2 from WGS and hydrogenated by-products are reduced. Most of the pyridine groups are quaternized by CH_3I , so that the $[\text{RhI}_2(\text{CO})_2]^-$ active species is maintained on the thermostable polymeric support,^{40,41} and the loss of rhodium by precipitation in the distillation section is reduced. Polyvinylbipyridine, called porous organic ligand (POL), obtained by polymerization of 6,6'-divinyl-2,2'-bipyridine, impregnated with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$ provides a support in which a single rhodium atom is σ -bonded to a pyridine ligand.⁴² This catalyst shows an excellent catalytic activity since at 195°C and 25 bar with a $\text{CH}_3\text{OH}/\text{CH}_3\text{I} = 1.4$ molar ratio, it provides a turnover frequency of 1558 h^{-1} in acetic acid (1.7 %) and methyl acetate (98 %), largely higher than the 312 h^{-1} value obtained for the homogeneous $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]/2,2'$ -bipyridine system.⁴²

In their early patent and publication on the noble metals catalysts, Monsanto^{16,17} described the activity of rhodium as well as of iridium. Even if the rhodium process was developed due to its higher activity, mechanistic studies were done on both systems. Clearly, it

appeared that with iridium the oxidative addition is not the rate determining step and on $[\text{IrI}_2(\text{CO})_2]^-$ (Fig. 1b) it occurs 100 times faster than on $[\text{RhI}_2(\text{CO})_2]^-$ due to the higher nucleophilicity of the iridium center.²³ At low iodide and water concentrations, neutral species operate in the catalytic cycle and the reaction of CH_3I gives the $[\text{IrI}_2(\text{CH}_3)(\text{CO})_2]$ complex. At higher iodide concentrations, anionic species analogous to those of rhodium are present and the oxidative addition of CH_3I produces the stable *fac,cis*- $[\text{IrI}_3(\text{CH}_3)(\text{CO})_2]^-$ complex²⁸ (Fig. 1c), which is the resting state. The migratory CO insertion is here the rate-determining step, since it is 10^{-5} slower than that observed for rhodium in non-protic solvents. Operating in methanol/water has a dramatic accelerating effect, presumably because the dissociation of an iodo ligand is solvent-assisted and gives the neutral intermediate $[\text{IrI}_2(\text{CH}_3)(\text{CO})_3]$. This complex evolves toward the acetyl $[\text{IrI}_2(\text{COCH}_3)(\text{CO})_2]$ species, the carbon atom of CO ligands being more electrophilic and more susceptible to the nucleophilic attack of the methyl group. British Petroleum Chemicals patented the use of various promoters able to act as the iodo-abstracting reagents in a catalytic manner. In particular, $[\text{RuI}_2(\text{CO})_3]^{43}$ (the $[\text{Re}_2(\text{CO})_{10}]$ rhenium promoter has also been patented⁴⁴) can efficiently react with $[\text{IrI}_3(\text{CH}_3)(\text{CO})_2]^-$ under CO to give $[\text{RuI}_3(\text{CO})_3]^-$ and $[\text{IrI}_2(\text{CH}_3)(\text{CO})_3]$. The reaction proceeds 800 times faster than in the absence of ruthenium.⁴⁵ At the present time, the Cativa™ process developed by BP Chemicals operates with Ir and Ru at 5 % w/w water, and the high concentrations of the resulting methyl acetate provides high reaction rates.^{25,26}

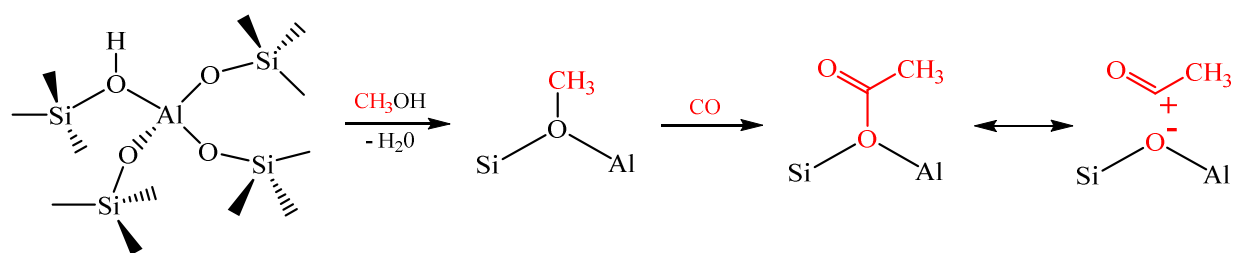
Today, many efforts are still delivered to convert methanol into acetic acid in very large industrial plants with the joint objectives to perform the carbonylation reaction under low pressures at reasonable temperatures, to recover and recycle easily the catalyst and to obtain high selectivity in order to simplify the purification process. Although cobalt and then rhodium and iridium complexes have been used to perform the industrial production of acetic acid with productivity as large as $1500 \text{ T}\cdot\text{day}^{-1}$, many studies are still conducted. The aim is to: i) still

improve the performances of the existing catalysts, ii) obtain attractive catalysts based on abundant and low price metals, iii) immobilize them on specific supports, and even iv) avoid metals and iodide promoters. In addition, some recent approaches involved the use of methanol produced from CO₂ and H₂, and carbonylate it starting from CO₂ as a CO surrogate. In this short review, we will analyze the more recent strategies, mainly developed during the last 10 years, metal by metal.

2. Heterogeneous catalysis with zeolites

Mordenite, a microporous silicoaluminate zeolite support with a strong acidity and hydrothermal stability, can catalyze the carbonylation reaction in the absence of metals. Large quantities of dimethylether are produced by dehydration of methanol on the acidic sites of H-Y zeolite, especially H-mordenite. Operating at 200 °C and 10 bar, Fujimoto and coworkers were the first to carbonylate dimethylether into methyl acetate.⁴⁶ This Koch reaction⁴⁷ involves adsorption and reaction of methanol or dimethyl ether on a Brønsted acid site, in the absence of halide cocatalyst to form the methoxy species (Scheme 2). This methoxy species reacts with CO to produce an acyl or acylium species, which reacts with H₂O to form acetic acid or methanol to form methyl acetate. As H₂O competes with CO for adsorption on the acidic sites, the dimethyl ether carbonylation preserves anhydrous conditions so that acidic mordenite was shown to reach 99% selectivity to methyl acetate at 150-190 °C.⁴⁸ It has been shown that this reaction occurs in the eight-membered ring channels (8-MR) of mordenite, whereas the 12-MR channels give rise to hydrocarbons, decreasing the selectivity in acetic acid and inducing catalyst deactivation.^{49,50} DFT calculations, molecular simulations, and reaction kinetics show that the 8-MR side pocket is the carbonylation reaction center, mainly because the methoxy group is parallel to the cylinder axis.^{51,52,53,54,55,56,57} *In situ* solid-state NMR spectroscopy and

DFT calculations are consistent with a covalent acetyl-zeolite $\text{Si}(\mu\text{-OC}(\text{OCH}_3))\text{Al}$ complex as reactive intermediate.⁵⁸



Scheme 2. Main steps for the activation of methanol on an acidic $\text{Si}(\mu\text{-OH})\text{Al}$ group and the carbonylation of the methyl group.

Introduction of Na^+ ions into the 8-MR channels followed by steam dealumination selectively removes the acidic sites in the 12-MR channels, so that the resulting mordenite presents a greater stability in the dimethyl ether carbonylation, and the deposition of coke is suppressed.⁵⁹

Recently the EU-12 zeolite (Edinburgh University-12) in its acidic form was prepared because it presents a unique framework topology with two-dimensional types of straight 8-MR channels along the *c*-axis. This zeolite was prepared by using a $\text{SiO}_2/\text{Al}_2\text{O}_3$ gel composition of 20, a $\text{Rb}_2\text{O}/(\text{Rb}_2\text{O}+\text{Na}_2\text{O})$ ratio of 0.7, and the (2-hydroxyethyl)trimethylammonium cation as structure-directing agent.⁶⁰ The dimethyl ether conversion into methyl acetate is maintained above 90 % for a conversion of 10 % during 30 h of reaction at 220°C and 30 bar, showing an attractive stability, largely higher than those of H-MOR or H-ZSM-35.⁶¹

Introduction of a small amount of zinc during the synthesis of mordenite (H-Zn-MOR) decreases the acid site concentration in the 12-MR channels, so that the deactivation of the catalyst in the carbonylation of dimethyl ether is slowed down and the coke deposition is

reduced. The conversion in methyl acetate **takes longer** than that of H-MOR, **since after 10 h it is still two times higher**.⁶²

To increase the mass transfer efficiency, introduction of polyethyleneglycol during the synthesis led to hierarchical MOR catalysts with an increase in their crystallinity and mass transfer efficiency. As strong acid sites slightly increased, the dimethyl ether conversion increased, and provided short reaction times were maintained, coke deposition was reduced.⁶³ Moreover, pretreatment of H-MOR with water at 300 °C for 10 min. enhances the conversion of dimethyl ether by 33 % and maintains the selectivity in methyl acetate at 99 %.⁶⁴

A recent stable metal-free catalyst was reported based on pyridine-modified H-mordenite zeolite.⁶⁵ Vapor-phase methanol carbonylation was conducted at 50 bar (0.5 % methanol - 99.5 % CO) to give methanol conversion of 100 % and acetic acid selectivity of 95 %. Little deactivation was observed during the 145 hours reaction.

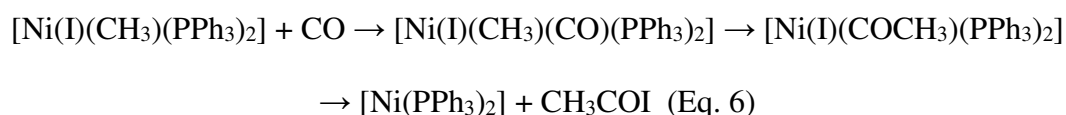
As we will shall see below, introducing a metal into the zeolite results in a significant increase in the catalytic reactivity to carbonylate methanol or dimethyl ether.

3. Catalysis with nickel

3.1 Homogeneous catalysis

Starting directly from $[\text{Ni}(\text{CO})_4]$, the simultaneous introduction of lithium acetate and potassium iodide entails the use of relatively low pressures (70 bar).⁶⁶ Using organophosphorus promoters, such as phosphine ligands, allows to decrease significantly the process conditions in the presence of hydrogen.⁶⁷ With an *in situ* Cylindrical Internal Reflectance Fourier Transformed Infrared (CIR-FTIR) reactor in [®]Hastelloy C, and operating at 160 °C and 62 bar of a CO/H₂ (4/1) pressure, Moser and coworkers showed that the NiI₂/LiI/PPh₃/MeI system

does not involve the **accumulation** of **observable** nickel carbonyl species.^{68,69} The active species $[\text{Ni}(\text{PPh}_3)_2]$ reversibly reacts with CH_3I in the rate limiting step to provide the $[\text{Ni}(\text{I})(\text{CH}_3)(\text{PPh}_3)_2]$ complex, which coordinates rapidly a CO ligand and evolves quickly toward the acetyl species, for which the reductive elimination reaction gives rise to acetyl iodide and regenerates the active species (Eq. 6).



Acetyl iodide reacts immediately with methanol to give methyl acetate or with water to form acetic acid. In fact, it is necessary that an equilibrium exists between the free phosphine ligand (15 % in this case) and the phosphonium $[\text{P}(\text{CH}_3)_3\text{I}]$ iodide. Interestingly, the $\text{P}(\text{t-Bu})_3$ phosphine induces higher reaction rates because its steric hindrance results in the $[\text{Ni}(\text{P}(\text{t-Bu})_3)_2]$ active species, and its higher basicity than PPh_3 accelerates the oxidative addition of CH_3I .⁶⁹ However, whereas the anionic $[\text{Ni}(\text{I})(\text{CO})_3]^-$ species is not detected in the solution, even in the presence of LiI , trace amounts of $[\text{Ni}(\text{CO})_4]$ are present, so that the toxicity of this complex is problematic in the industrial process.

Promoters of $\text{Ni}(\text{OAc})_2$, such as tin derivatives, SnPh_4 for instance,⁷⁰ or molybdenum or tungsten salts and trialkylamines or phosphines,⁷¹ allow to operate the carbonylation reaction at lower pressure (30 bar). Introduction of small partial pressure of dihydrogen maintains the stability of the $\text{Ni}/\text{Mo}/\text{LiI}/\text{PPh}_3$ catalytic system.⁷²

3.2 Heterogeneous catalysis

Nickel deposited from the halide, nitrate, acetate or acetylacetonate precursors on activated carbon (AC) was shown by Fujimoto and co-workers to catalyze the carbonylation of

methanol.⁷³ It is necessary to operate in the presence of methyl iodide, and at 300 °C and 11 bar in a continuous flow reactor. Thus, 70 % of acetic acid and 22 % methyl acetate are produced with small amounts of methane, dimethyl ether and CO₂.^{73,74} When using methyl bromide, on Fe/AC or Co/AC catalysts, lower performances are obtained. Similarly, starting from methyl chloride leads to its carbonylation into acetic acid and methyl acetate with a 89 % selectivity, provided some methyl iodide is present as promoter.⁷⁵ Increasing the CO/methanol ratio to 5 in the feed, results in a 95 % yield in acetic acid and in the absence of by-products.⁷⁶ Kinetic analyses are consistent with a methanol conversion in two parallel pathways: i) carbonylation to methyl acetate, and ii) dehydration into dimethyl ether that is further carbonylated in methyl acetate.⁷⁷ Acetic acid results from the hydrolysis of this ester or through its carbonylation into acetic anhydride, even if a higher pressure of 30-50 bar is necessary to reach a 50-70 % selectivity.^{78,79,80} Dimethyl ether was shown to be carbonylated into methyl acetate with a 90 % selectivity, **and a small amount** of water **accelerates** the methyl iodide adsorption.⁸¹ In addition, methyl iodide has the property of re-dispersing the nickel particles with 2.2 nm average diameter on activated carbons through the formation of NiI₂.⁸² The dispersion of Ni on AC is 89 % at 1% w/w nickel loading.⁸³ These performances are largely higher than those obtained on polymer or silica gel (at high pressures),⁸⁴ and zeolites supports.^{74,76} In the flow process, surface carbon deposition and aggregation of nickel particles reduce the reactivity of the catalyst, which can be regenerated by treatment under hydrogen at 400 °C.⁸⁵ The mechanism of deactivation involved a strong adsorption of methanol and reaction products that plugs the catalyst micropores and leads to diffusion limitations. In that context, the use of AC with limited microporosity should be encouraged in order to limit deactivation.⁸⁶ The formation of inactive nickel carbide species has also been reported.⁸⁷ Interestingly, it was also evidenced that the surface oxygen-containing groups of AC contribute to limit the accumulation of carbonaceous deposits on the Ni/C catalyst.⁸⁸ A small reduction of methane

yield (~2 %) to increase the selective carbonylation of methanol can result from the introduction of equimolecular amounts of tin to nickel (Ni-Sn/AC catalyst).⁸⁹ Addition of palladium to nickel or nickel/copper catalysts supported on AC allows to operate continuously under 1 bar at 300 °C and to obtain a 65 % methanol conversion with a selectivity of 80 % in acetic acid and methyl acetate. During 200 h experiments, the catalytic activity was constant and no loss of nickel or palladium was detected.⁹⁰ However, catalyst deactivation was reported for a Ni-Pd/C catalyst operating at 260 °C and 15 bar.⁹¹ The strong adsorption of the reaction products plugs the pores, leading to diffusion limitations, Ni migration on the surface and resulting in easy carbon deposition, which enhances the deactivation. Regeneration of the catalyst with H₂ at 400 °C restores the activity, although the deactivation rates after this treatment are higher.

More recently, porous carbon beads (PCB) have been prepared by carbonization of polyvinyl chloride, and thanks to the porosity of this support, highly dispersed nickel particles were formed, after reduction with hydrogen at 350 °C. This Ni/PCB catalyst catalyzes the carbonylation of methanol into acetic acid at 220 °C and 10 bar. These catalysts are more thermally stable than those produced on AC. With an effective radius of 3.54 nm for the spherical Ni particles, the activity is 47.7 mmol_{MeOH}.mol_{Ni}⁻¹.s⁻¹. This activity is enhanced to 60 mmol_{MeOH}.mol_{Ni}⁻¹.s⁻¹ by addition of lanthanum as promoter.⁹²

Catalysis with nickel has also been explored in the absence of iodide promoter. On a silica-alumina support, treated at 325 °C with a H₂S/H₂ mixture, nickel or nickel-molybdenum oxides were deposited; this sulphided catalyst carbonylates dimethyl ether with CO/H₂ at 64 bar and 240 °C, giving methylacetate and ethanol, with few amounts of methyl formate and propanol.^{93,94} A second example is described in a recent patent where a nickel salt, for instance nickel acetate dissolved in dilute hydrochloric acid or ethanol, impregnates a support such as silica, alumina or AC, under ultrasonic activation. The reduction is carried out under an

alkane/hydrogen mixture flow from 300 to 1000 °C. These heterogeneous Ni catalysts carbonylate methanol at 100-400 °C under 10-120 bar CO pressure, in the absence of any iodide source, and show a conversion rate of 84% and a selectivity in acetic acid/methyl acetate of 86%.⁹⁵

Thus, the objective to operate the carbonylation of methanol avoiding the presence of any iodide could be accomplished, provided the loss of $[\text{Ni}(\text{CO})_4]$ in the process and its recycling could be precisely stated.

4. Catalysis with copper and gold

4.1 Heterogeneous catalysis

Impregnating activated carbon with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ results in the supported CuCl_2/AC catalyst with a specific surface area of $1000 \text{ m}^2 \cdot \text{g}^{-1}$ and particle sizes of 20-40 mesh that operates in a continuous flow reactor at atmospheric pressure.⁹⁶ At 300 °C the carbonylation of methanol is characterized by a 30 % conversion and a 78 % selectivity in methyl acetate, whereas the 10% NiCl_2/AC catalyst shows a 43.3 % conversion of methanol. The authors have studied the carbonylation reaction and showed that the mixed system $\text{NiCl}_2\text{-CuCl}_2/\text{AC}$ has high activity and stability. Particularly for the 5%Ni-15%Cu catalyst, at 300 °C, a conversion of 34.5 % is obtained with a selectivity of 94.7 % in methyl acetate, 5.7 % of dimethyl ether and ~ 0.1 % of methane.

Copper containing mordenite catalysts (Cu-MOR) carbonylate methanol into acetic acid and methyl acetate with a global selectivity higher than 70 % at 350 °C and 25 bar in the absence of halogens, with performances being close to those of H-MOR.^{97,98} A first period of ~3 h is observed where the reaction mainly leads to hydrocarbons, especially for H-MOR, followed by

the carbonylation into acetyls. Pretreatment in CO at 350 °C or addition of a small amount of palladium improve the yields. Mechanistic studies conducted by the group of Corma have shown that a different reaction mechanism occurs on H-Mordenite and Cu-H-Mordenite.^{51,52} In the presence of H-Mordenite, the reaction is slow and acetic acid is formed as a primary acetyl product, while on Cu-H-Mordenite the reaction is fast and methyl acetate is produced. The reaction mechanism on Cu-H-Mordenite involves two neighboring sites, one bridged hydroxy and a neighboring Cu⁺. The Brønsted acid site is responsible for activating the methanol, while Cu⁺ could activate the CO, and adsorbs preferentially the DME compared to methanol and water. Other authors proposed that: i) the Cu⁺ species enables the stabilization of dimethyl ether,⁹⁹ or ii) strong electrostatic interaction with a nucleophilic CH₃⁺-CO intermediate,⁵⁶ and iii) that the CO on Cu⁺ site is not an active species to produce either methyl acetate or acetic acid. Cu/TiO₂-SiO₂ catalysts were also reported to be active in the halide free vapor phase carbonylation of methanol.¹⁰⁰

In addition, mordenite, on which 15% CuCl₂ and 5% NiCl₂ have been deposited, presents an interesting catalytic activity in the absence of any iodide source. Operating at 15 bar and 350 °C, in a flow process, the conversion of methanol reached 84 % and the selectivity in acetic acid and methyl acetate 62 %.^{101,102}

The synthesis of acetic acid with the exclusive use of methanol reactant has been also explored. It uses a Pd/CeO₂ catalyst to generate *in situ* CO from methanol decomposition at 300 °C that reacts with methanol on a copper-mordenite catalyst to produce acetic acid and methyl acetate. Due to the coproduction of H₂ in the first catalytic step, Cu/MOR needs to be hydrogen tolerant, and it is the case. This catalytic system does not require any halide as promoter.^{103,104}

Eastman Chemical Co patented in 2000 the vapor-phase carbonylation of methanol into acetic acid and methyl acetate using gold deposited on carbon or activated carbon (1% Au/C)

in the presence of methyl iodide operating at 240 °C and 17 bar of CO/H₂.^{105,106} Their activity is close to that of iridium catalysts. XRD analyses show that the gold particles have a diameter of 12 and 28 nm for the two catalysts prepared.¹⁰⁷ Due to the presence of CH₃I during the carbonylation reaction, small clusters of gold were observed containing 2 and 3 atoms stabilized by iodide, (Au₂I)^{δ+} and (Au₃I₂)^{δ+}. In addition, *in-situ* infrared investigations on TiO₂-supported gold, which act as catalysts for the carbonylation of CH₃OH/CH₃I, revealed gold carbonyls, formed by CO adsorption on the surface, that react with neighboring methoxy species bonded to Ti⁴⁺ sites.¹⁰⁸

5. Catalysis with cobalt

5.1 Homogeneous catalysis

At high pressure (500-700 bar), and at 250 °C the CoI₂ precursor is reduced in the presence of water and CO.^{109,29,3,27} The [Co₂(CO)₈] complex and hydrogen iodide are formed. *In situ* generation of CH₃I occurs from methanol and HI. [Co₂(CO)₈] reacts with CO and H₂O to provide [Co(H)(CO)₄] and CO₂. The nucleophilic attack of [Co(CO)₄]⁻ on CH₃I results in the formation of [Co(CH₃)(CO)₄] and HI. The CO migratory insertion, the rate determining step, provides the acetyl species [Co(COCH₃)(CO)₃], and under CO pressure, [Co(COCH₃)(CO)₄]. Water reacts with this latter species to regenerate [Co(H)(CO)₄] and produce CH₃COOH.^{109,110} However as the [Co₂(CO)₈] complex disproportionates in methanol into Co^I and Co^{-I} species and generates [Co(CO)₄]⁻,^{111,112,113} the **same** catalytic cycle involving **as a first step the** CH₃I oxidative addition to this **anionic** species can also be considered, leading to [Co(CH₃)(CO)₄] and I⁻. The hydrolysis step on [Co(COCH₃)(CO)₄] regenerates [Co(CO)₄]⁻ and leads to CH₃COOH + H⁺.²⁷ In the earlier studies on the methanol carbonylation into acetic acid¹¹⁴ or methylacetate into acetic anhydride,¹¹⁵ Reppe and Friederich described the positive effect of

ammonium or phosphonium iodides. Presumably, this anionic pathway should prevail, since pyridine has been demonstrated to accelerate the rate, by a factor of around 400, by reacting with the acyl species to give the $[\text{C}_5\text{H}_5\text{NCOCH}_3]^+[\text{Co}(\text{CO})_4]^-$ intermediate.¹¹⁶ An infrared study has shown that this species reacts with methanol to give methyl acetate and $[\text{C}_5\text{H}_5\text{NH}]^+[\text{Co}(\text{CO})_4]^-$. Similarly, with the large countercation $[\text{PPN}]^+$ the anionic $[\text{Co}(\text{I})(\text{COCH}_3)(\text{CO})_3]^-$ complex has been isolated and fully characterized and its formation is considered as resulting from the addition of $[\text{PPN}]\text{I}$ to the $[\text{Co}(\text{COCH}_3)(\text{CO})_3]$ species.¹¹⁷

Even if addition of phosphine ligands, ionic iodides, starting from magnesium carbonyl cobaltate or adding a palladium or a platinum co-catalyst^{118,119} lead to significant improvements in the reaction conditions, particularly the pressure (200 bar), the gain was not sufficient with regard to the rhodium system. More recently, the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2]/\text{PEt}_3/\text{H}_2\text{O}/\text{MeI}$ system was shown to operate at 100 bar and 120-140 °C with a catalytic activity in acetic acid/methyl acetate, which is 1.5 times higher than the rate using rhodium (turnover frequency 314 h⁻¹, compared to 188 h⁻¹, even if the concentration of cobalt is 30 times that of rhodium).^{120,121} Whereas $[\text{PMeEt}_3]\text{I}$ is expected to be formed in the medium, free phosphine ligand is present in the solution, and the complex $[\text{Co}(\text{I})(\text{CO})_2(\text{PEt}_3)_2]$ has been isolated and fully characterized after catalysis. Moreover the analogous complex $[\text{Co}(\text{I})(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ has a modest activity.¹²¹ Synthesis of the bidentate $\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PEt}_2$ ligand and its coordination to cobalt in order to form the $[(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{PEt}_2)\text{Co}(\text{CO})]$ complex, results in a precursor, which is inactive in the methanol carbonylation reaction, and which is decomposed as shown by high pressure ³¹P NMR studies, presumably because of phosphine oxidation and/or quaternization.³⁵ Bi- to quadridentate 1,3-dioxolane and 1,4-dioxane phosphine ligands have also been investigated.¹²² In combination with CoI_2 , $\text{PhP}(\text{CH}_2\text{C}_4\text{H}_7\text{O}_2)_2$ and $[-\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{C}_4\text{H}_7\text{O}_2]_2$ lead to methanol conversions of 95 %, and selectivity to methyl acetate and acetic acid of 33 %

and 60 %, respectively, at 160 °C and under 200 bar.

5.2 Heterogeneous catalysis

Deposition of cobalt on zeolites from $\text{Co}(\text{NO}_3)_2$ solutions and calcination at 500 °C produce a catalyst that allows one to carbonylate methanol in the presence of halide promoters at 180 °C and 700 bar with a conversion of 73 % in 42 h into 43 % methyl acetate, 10.6 % acetic acid and 17.3 % dimethylether.¹²³ With the aim to avoid corrosive catalytic materials, the carbonylation of methanol into methylacetate was performed at 140 °C and 740 bar in the absence of any iodide source, using $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}(\text{H})(\text{CO})_4]$ with a small H_2 partial pressure in the CO gas.¹²⁴

6. Catalysis with rhodium

6.1. Homogeneous catalysis

Even if the homogeneous rhodium catalysts lead to high selectivity in acetic acid of 99% and impressive turnover numbers, many studies are carried on to further improve the reaction rates by substitution of a CO ligand by a more nucleophilic ligand to accelerate the oxidative addition of CH_3I . Thus, operating at 150 °C and 27 bar in the presence of 17 % water, the $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$ precursor is characterized by an almost double carbonylation rate than $[\text{RhI}_2(\text{CO})_2]^-$.¹²⁵ The oxidative addition of CH_3I is 57 times faster at 25 °C whilst the migratory CO insertion is 38 times slower for the neutral PEt_3 complex. However, oxidative addition of HI to form $[\text{Rh}(\text{H})\text{I}_2(\text{CO})(\text{PEt}_3)_2]$ and then $[\text{RhI}_3(\text{CO})(\text{PEt}_3)_2]$ leads to the reductive elimination of $[\text{PEt}_3\text{I}]^+$, which is hydrolyzed to give PEt_3O .¹²⁶ The $[\text{RhI}_2(\text{CO})_2]^-$ active species is progressively reformed. The same degradation prevails with the carbene ligand (NHC) present in the $[\text{RhI}(\text{CO})(\text{NHC})_2]$ complex.¹²⁷ The higher σ -donating properties of the carbene ligands, which should accelerate the oxidative addition step is offset by the steric constraints created by

the *N*-alkyl substituents. Haynes, Cole-Hamilton and co-workers have prepared bidentate ligands in which the PR₂ moiety is bonded to a cyclopentadienyl ligand.³⁵ Thus, the two [(η⁵-C₅Me₄(CH₂)₂PEt₂)Rh(CO)] and [(η⁵-C₅Me₄(CH₂)₂PPh₂)Rh(CO)] complexes present an activity in the methanol carbonylation reaction similar to that of [RhI₂(CO)₂]⁻ especially for the last one. The highest nucleophilicity of the rhodium center accelerates the oxidative addition of CH₃I; the reductive elimination of CH₃COI is however the rate limiting step. Over time, the catalyst is transformed into the inactive complex [(η⁵-C₅Me₄(CH₂)₂PEt₂)RhI₂].

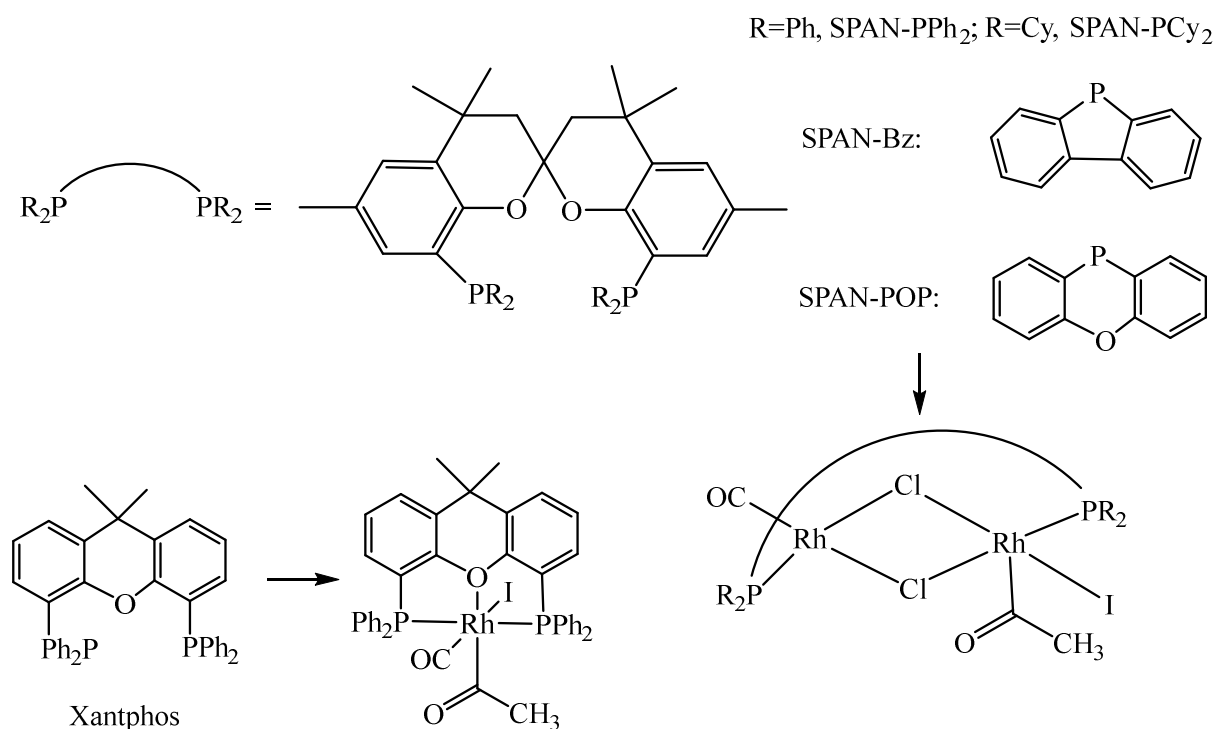
The bidentate Ph₂PCH₂P(S)Ph₂ \widehat{PS} ligand promotes the rhodium catalyzed methanol carbonylation under industrially relevant conditions,¹²⁸ and at 50 % methanol conversion (185 °C, 70 bar), the mononuclear [RhCl(CO)(\widehat{PS})] complex increases the rate of [RhI₂(CO)₂]⁻, (generated from [Rh₂(μ-Cl)₂(CO)₄]), from 2.3 to 19.6 mol.l⁻¹.h⁻¹.¹²⁹ This \widehat{PS} ligand not only increase the rate of the oxidative addition step and the stability of the complex, but also, as shown by DFT calculations, accelerates the migratory CO-insertion due to its π-donor capability.¹³⁰ The complex [Rh₂(μ-S)-CH₂CH₂PPh₂](CO)₂] increases the maximum turnover rate of [RhI₂(CO)₂]⁻ from 450 to 1800 h⁻¹.¹³¹ A similar value of 1600 h⁻¹ has been observed when the -CH₂CH₂- chain between the two phosphorus and sulfur atoms is replaced by a bulky *o*-carborane backbone to provide the *S,P*-SC₂B₁₀H₁₀PPh₂ ligand.¹³² The two thioether-phosphine ligands Cy₂PCH₂CH₂SPh and Cy₂PCH₂CH₂SEt (Cy=cyclohexyl, \widehat{PSPh} and \widehat{PSEt}) have been synthesized and the complexes [RhCl(CO)(\widehat{PSPh})] and [RhCl(CO)(\widehat{PSEt})] present a higher activity (7.13 and 2.81 mmol in 1h at 120 °C and 32 bar) than [RhI₂(CO)₂]⁻ (2.78 mmol).¹³³

Density functional studies have been carried out on the steps of the catalytic carbonylation cycle,^{134,135,136,137} and in a further approach, the solvent effects have been included.¹³⁸ Thus, in methanol the free energy of activation ΔG[‡] is 26.9 kcal.mol⁻¹ in good

agreement with the experimental estimate of 22.9 kcal.mol⁻¹. For the rate-determining step of the S_N2 oxidative addition of CH₃I to the rhodium(I) complex, the ΔG values, calculated in methanol solutions, are 11.8 for [RhI₂(CO)₂]⁻, 8.7 for [RhI(CO)(Ph₂PCH₂CH₂PPh₂)₂], 5.7 for [RhI(CO)(Ph₂PCH₂P(S)Ph₂)₂], 2.5 for *trans*-[RhI(CO)(PEt₃)₂], and 1.3 kcal.mol⁻¹ for [RhI(CO)(*S,P*-SC₂B₁₀H₁₀PPh₂)⁻].¹³⁸

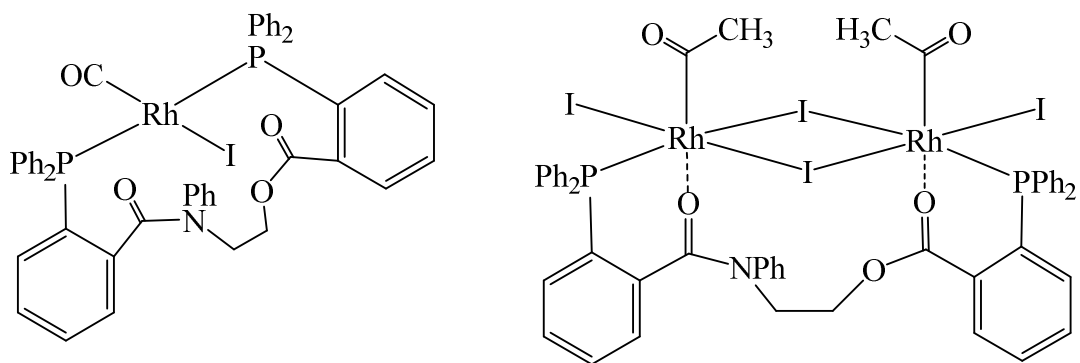
The three ligands Ph₃P=O, Ph₃P=S, and Ph₃P=Se, added to the [Rh₂(μ-Cl)₂(COD)₂] precursor, increase significantly the carbonylation rate of methanol.¹³⁹ Then Dutta and co-workers explored the reactivity of mononuclear rhodium complexes bearing chelating nitrogen or phosphine containing ligands, where acetyl-, benzoyl-, carboxaldehyde-, furyl-, carboxylic acid- substituents allowing to produce a $\widehat{\text{N}}\text{O}$ or a $\widehat{\text{P}}\text{O}$ coordination. The reactivity is ~50-70 % higher than that of [RhI₂(CO)₂]⁻.^{140,141,142,143,144,145} In these [RhI(CO)(bidentate)] complexes, the greater nucleophilicity than [RhI₂(CO)₂]⁻ is responsible of the higher rate for the oxidative addition. Exploring the reactivity of the Ph₂PCH₂P(S)Ph₂ ligand Haynes *et al.* observed that the oxidative addition of CH₃I has a rate constant of 1.19 x 10⁻³ M⁻¹.s⁻¹ at 25 °C. It is similar to the rate of the corresponding [RhI(CO)(dppe)] (dppe = Ph₂PCH₂CH₂Ph₂) complex of 1.41; however the migratory CO insertion is 6.2 x 10⁻¹ s⁻¹ for the $\widehat{\text{P}}\text{S}$ ligand, whereas is 1.6 x 10⁻⁴ s⁻¹ for dppe, *i.e.* 3000 times faster, due to a significant steric strain.¹⁴⁶ Moreover, as most of the previous ligands are unsymmetrical, Pringle, Sunley *et al.* have shown that such diphosphine ligands generate mononuclear [RhI(CO)(Ph₂PCH₂CH₂PAR₂)] rhodium complexes, for which the carbonylation reaction is certainly lower than with [RhI₂(CO)₂]⁻ but the longevity is greater than any rhodium-phosphine catalyst in the industrial process conditions.^{147,148} The addition of bi- and polydentate ligands having a large bite angle to rhodium or iridium leads to efficient carbonylation catalysts. Particularly interesting is the observation that in the presence of hydrogen the formation of acetaldehyde is significantly reduced, even if large amounts of methane are produced.^{149,150} The mechanism by which the Xantphos ligand (Scheme 3)

coordinates to rhodium has been more particularly analyzed in the various steps of the carbonylation reaction.¹⁵¹ In the Rh(I) complex, the ligand adopts a κ^3 -P,O,P coordination mode with the two phosphorus atoms in *trans*-position, to give $[\text{RhI}(\text{CO})(\kappa^3\text{-Xantphos})]$. Oxidative addition of CH_3I provides the cationic methyl intermediate $[\text{RhI}(\text{CH}_3)(\text{CO})(\kappa^3\text{-Xantphos})]^+$, which evolves rapidly towards the acetyl neutral Rh(III) species $[\text{RhI}_2(\text{COCH}_3)(\kappa^3\text{-Xantphos})]$. With this catalyst precursor the turnover number into acetic acid and methyl acetate is 1585 against 1000 for the usual $[\text{RhI}_2(\text{CO})_2]^-$ complex (130 °C, 20 bar).¹⁵² For the SPAN-diphosphine ligands, the two phosphorus atoms coordinate the rhodium metal center in *trans*-position, and there is no interaction of the two oxygen atoms with Rh. The $[\text{RhCl}(\text{CO})(\kappa^2\text{-SPAN-PPh}_2)]$ complex does not react with CH_3I , except for giving the iodo analog $[\text{RhI}(\text{CO})(\kappa^2\text{-SPAN-PPh}_2)]$ by halide metathesis. However, the $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_2(\kappa^2\text{-SPAN-PPh}_2)]$ precursor reacts with CH_3I to provide by oxidative addition and then migratory CO-insertion the Rh(I)-Rh(III) $[\text{Rh}_2(\mu\text{-Cl})_2\text{I}(\text{COCH}_3)(\text{CO})(\kappa^2\text{-SPAN-PPh}_2)]$ complex, shown in Scheme 3. Steric constraints are presumably at the origin of the absence of oxidative addition. These precursors are active in the carbonylation of methanol, with best results observed for SPAN-POP giving rise to a TON of 766 and a TOF of 2299 h^{-1} , instead of 190, and 762 h^{-1} for $[\text{RhI}_2(\text{CO})_2]^-$ (150 °C, 22 bar at 22°C, 18 min and 15 min, respectively).¹⁵³ DFT calculations confirm the $\text{S}_{\text{N}}2$ character of the approach of one Rh center to CH_3I of the bridging diphosphine dinuclear complex, and the activation barrier for this rate-determining step is 5.5 $\text{kcal}\cdot\text{mol}^{-1}$.¹⁵⁴



Scheme 3. Acetyl complexes resulting from the oxidative addition of CH₃I to rhodium complexes containing large bite angle bidentate ligands (adapted from ref.^{153,154}).

Disymmetric diphosphine ligands have been introduced in the rhodium coordination sphere and the two Ph₂PC₆H₄ moieties bonded by a -COXCH₂CH₂OOC- linker (X=O, NH or NPh) provide mononuclear *trans*-[RhCl(CO)(diphos)] complexes, in which the two phosphorus atoms are in *trans*-positions (Scheme 4).¹⁵⁵ With the mononuclear complex of Scheme 4, carbonylation of methanol at 170 °C, 22 bar and for 15 min, a TON of 803 is reached, whereas the TON of [RhI₂(CO)₂]⁻ is 381. Recycling of the catalytic mixture gives the same activity throughout several runs. The *cis*-dimeric complex and its *trans*-isomer have been identified after catalysis by infrared and ³¹P NMR; they can be obtained directly from the monomeric complex by addition of CH₃I. They are considered as a reservoir for the mononuclear active species.^{156,157}



Scheme 4. Acetyl complexes resulting from the oxidative addition of CH_3I to rhodium complexes containing large bite angle bidentate ligands (adapted from ref. ^{155,156,157}).

In addition to these complexes, many rhodium precursors containing chelating ligands have been reviewed by Süß-Fink¹⁵⁶ and Haynes²⁶ that show higher catalytic performances in **water-rich reaction mixtures** than the classical Monsanto catalyst, even a lot of them are transformed into inactive species, especially at high temperatures or **due to decoordination of a phosphorus atom and formation of a quaternized phosphine moiety**.^{158,159,160}

Interestingly, we can mention the tris-nitrogen containing ligand, 1,8-diphenylimino-3,6-dimethylcarbazolide, which provides the neutral $[\text{Rh}(\text{CO})(\widehat{\text{N}}\widehat{\text{N}}\widehat{\text{N}})]$ complex, reacting with CH_3I 50 000 times faster than $[\text{RhI}_2(\text{CO})_2]^-$.¹⁶¹ **However, no evidence was found for migratory CO insertion to give the corresponding acyl species.**

To reduce simultaneously the amounts of water and LiI in the medium, some promoters like $\text{Zn}_3(\text{PO}_4)_2$, NiCl_2 , FeCl_3 , heteropolyacids (HPA) such as $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$, chromium, vanadium or lanthanide salts, can be added to the rhodium precursor and increase the stability of the catalyst and the carbonylation rates.^{162,163,164,165,166}

6.2. Heterogeneous catalysis

Beyond the polyvinylpyridine resins of the AceticaTM process, polymerisation of tris(styryl)phosphine leads to a solid containing phosphine ligands, called POL-PPh₃. Impregnation of [Rh₂(μ-Cl)₂(CO)₄] allows to immobilize Rh; the resulting Rh-POL-PPh₃ catalyst exhibits higher activity than [RhI₂(CO)₂]⁻ at 195 °C and 25 bar (TOF = 1550 h⁻¹) with a near stable activity for 180 h.¹⁶⁷ Similarly, the Rh-POL-2Bipy system containing the bipyridine ligand presents a high surface area and a high thermal stability, and turnover frequencies as high as 1400 h⁻¹ for near 400 h were obtained at 195 °C and 25 bar.⁴² Another approach consists in using Ionic Liquids (IL) to maintain the rhodium catalyst in the ionic liquid phase. Thus, 3-butyl-1-methylimidazolium bis(trifluoromethylsulfonyl)amide,¹⁶⁸ or 1-butyl-3-methylimidazolium iodide¹⁶⁹ IL, eventually impregnated on a silica support (Supported Ionic Liquid Phase)¹⁷⁰ allowed to perform a continuous process, to separate easily the reaction products, and also to stabilize the rhodium anionic species. N-butyl- or N-hexamethylimidazolium ILs with the dihydrogenophosphate and hydrogenocarbonate anions induce higher reactions rates, with the [Rh/CH₃I] system.¹⁷¹

As soon as 1972, Roth and coworkers, from Monsanto, reported the vapor phase methanol carbonylation reaction performed with a Rh solid catalyst prepared by impregnation of activated carbon with the catalyst solution employed in the liquid phase carbonylation system.¹⁷² In this case, also, the reaction was first order in methyl iodide and independent of methanol and carbon monoxide concentrations. The methanol conversion of 64 % remained constant during experiments of 1000 h, so that the heterogeneous approach paralleled that one of the homogeneous process. In addition, this process requires significantly lower pressures (~10-15 bar) than the industrially applied homogeneous technologies (~30 bar).¹⁷³

Recently, graphitic carbon nitride, g-C₃N₄, was reacted with rhodium nitrate to incorporate rhodium particles on the support and obtain Rh(x)-g-C₃N₄ (where x represents the rhodium content). For x=1 and 3, the nanoparticles are well dispersed and the conversion of methanol into acetic acid and methylacetate is 99.9 % at 40 bar and 140 °C, the rhodium leaching being 0.5 and 1.1 %, respectively.^{174,175,176} Presumably the reaction involves in a first step the formation of dimethyl ether and methyl acetate, which are converted to acetic acid, and no methane nor acetaldehyde and propionic acid are formed.¹⁷⁷ Other metallic heterogenized catalysts have been also prepared, such as Al/g-C₃N₄, Ir-, Co-, and Pd/g-C₃N₄ and all of them present a higher methanol conversion and acetic acid selectivity than those supported on tungsten carbide or Fe₃O₄. Beside Rh/g-C₃N₄ the rhodium complex containing the 3-benzoylpyridine ligand supported on Pd/g-C₃N₄ appears as a promising catalyst.¹⁷⁸ A Rh molecular catalyst immobilized on a charged 1,3-bis(pyridyl)imidazolium-based covalent triazine framework shows high stability in plug flow reaction in gas phase, affording a TOF of 3693 h⁻¹ and a productivity of 218.9 mol.kg⁻¹.h⁻¹ for acetyl products.¹⁷⁹

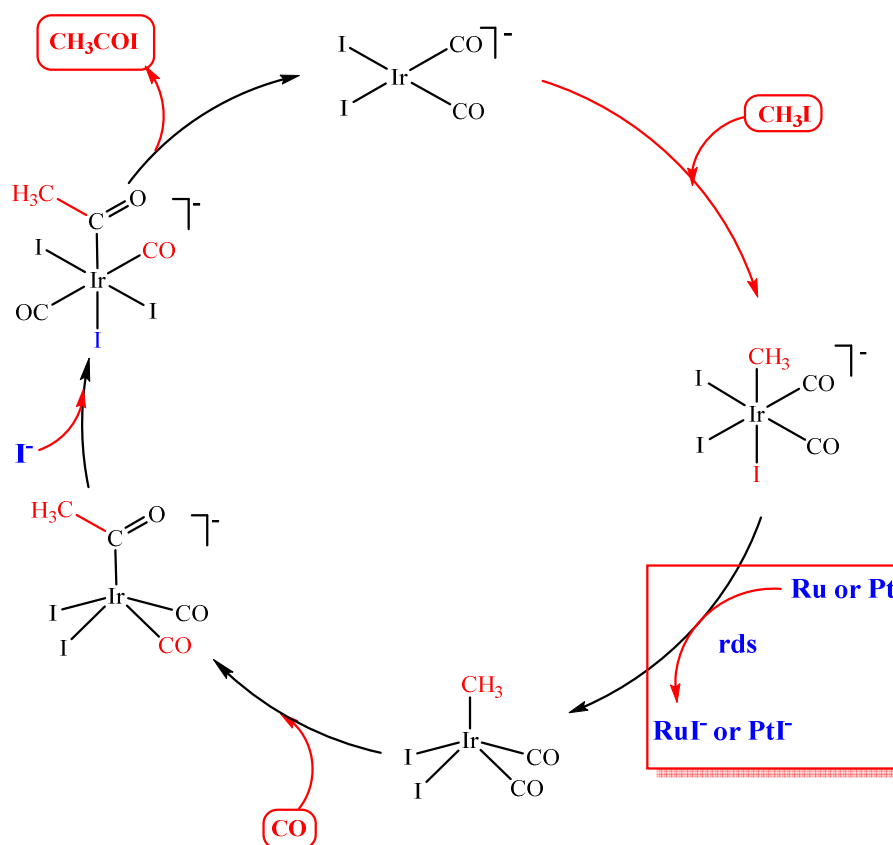
The [Rh₆(CO)₁₆] cluster can be used to prepare TiO₂-supported rhodium catalysts and spectroscopic investigations have clearly shown that only the terminal methoxy groups bonded to a single titanium atom are effective for producing methylacetate and dimethylether at 140-170 °C.¹⁸⁰ Montmorillonite functionalized by (3-aminopropyl)trimethoxysilane and reacted with a quinolone carboxylic acid provides a nitrogen-containing ligand linked to a RhCl(CO)₂ fragment. This rhodium catalyst supported on modified montmorillonite can carbonylate methanol with a 99.9 % conversion at 130 °C and 20 bar with a 99.9 % selectivity in acetic acid. No leaching of rhodium was detected and the catalyst, recovered by simple filtration can be reused without any loss of efficiency.¹⁸¹

Finally, selective methanol carbonylation to acetic acid could be achieved over an atomically dispersed Rh/ZrO₂ catalyst in a gas phase, halide-free process by support acidity.¹⁸² By poisoning acidic sites of the support, the overall process selectivity reached ~54% at a stoichiometric methanol to CO feed ratio (200-300 °C, atmospheric pressure).

7. Catalysis with iridium

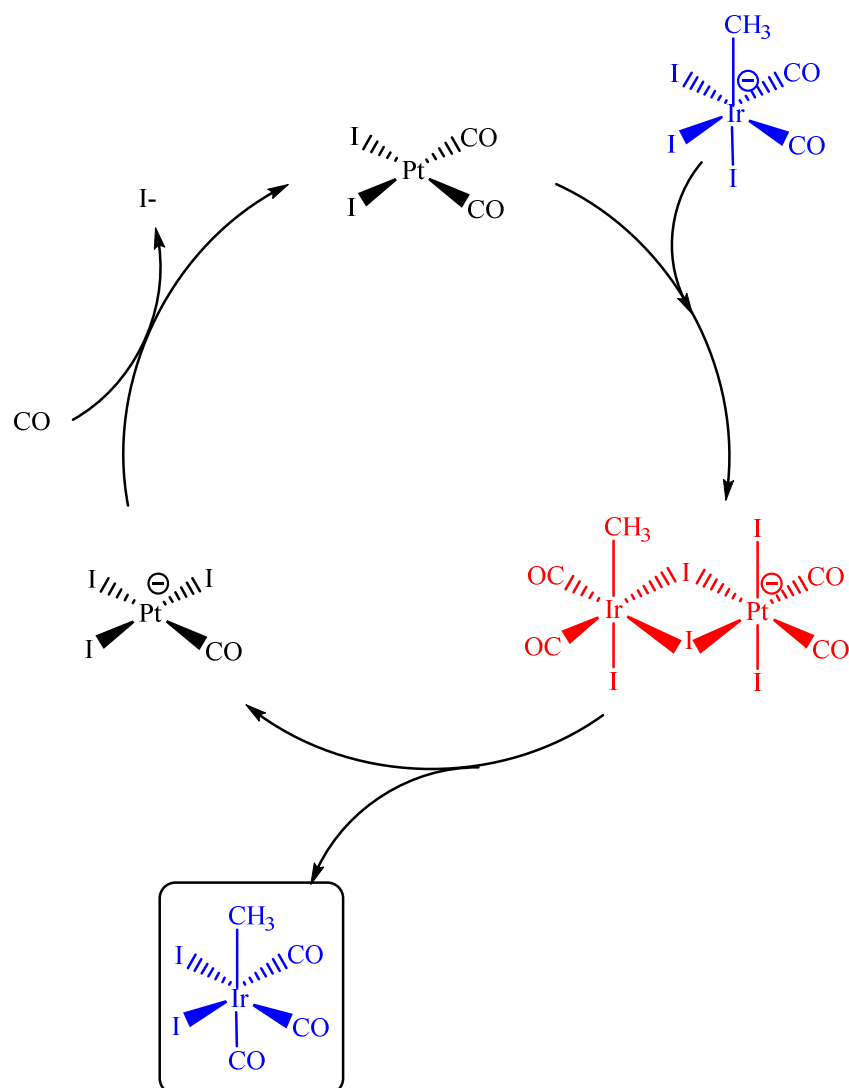
7.1. Homogeneous catalysis

In addition to the Cativa™ process operating with Ir and Ru at 5 % w/w water, for which the high concentrations of the resulting methyl acetate provides high reaction rates,^{25,26} an analogous cooperative effect between [IrI₂(CO)₂]⁻ and [PtI₂(CO)]₂ has been observed.¹⁸³ The main role of the platinum promoter is to abstract an iodide ligand from [IrI₃(CH₃)(CO)₂]⁻ as represented for Ru and Pt on Scheme 5.



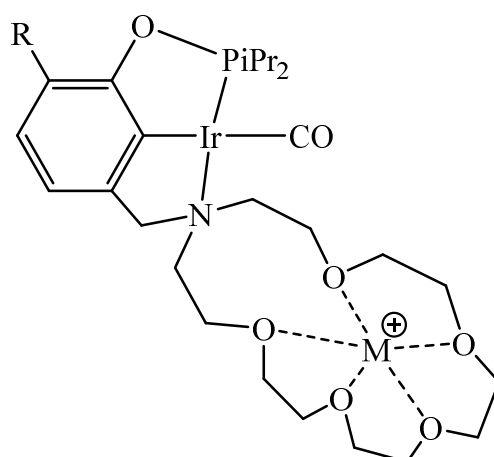
Scheme 5. Catalytic cycle of $[\text{Ir}_2(\text{CO})_2]^-$ at low water contents assisted by ruthenium or platinum complexes.

In the case of platinum, this I^- abstraction proceeds *via* a (di- μ -iodo)iridium-platinum dinuclear intermediate species, as analyzed under CO with the $[\text{PPN}]^+$ counter-cation.¹⁸⁵ This complex generates the neutral $[\text{Ir}_2(\text{CH}_3)(\text{CO})_3]$ complex and the anionic $[\text{PtI}_3(\text{CO})]^-$ species which regenerates $[\text{PtI}_2(\text{CO})_2]$ with the loss of I^- (Scheme 6).



Scheme 6. Detailed pathway of the reaction of platinum on the $[\text{IrI}_3(\text{CH}_3)(\text{CO})_2]^-$ intermediate species (adapted from ref.¹⁸⁴).

In a recent approach, iridium complexes containing aza-crown macrocycles such as the aza-18-crown-6 one shown on Scheme 7 can incorporate a promoter such as Li^+ , K^+ , Hf^+ , especially in the presence of a tetrabutylammonium salt, which plays itself a promoting and a phase transfer mediator role. Bridging the primary and second coordination sphere accelerates the carbonylation reaction through the removal of the I ligand after the oxidative addition of CH_3I .^{184,185,186}



Scheme 7. Iridium pincer-crown ether complexes where a M salt improve the methanol carbonylation rate (adapted from ref.^{184,185,186}).

7.2. Heterogeneous catalysis

Interestingly, and as in the case of Rh catalysts, carbon supported Ir catalyst have also shown interesting performances for the vapor phase methanol carbonylation.^{188,189,190,191} In this catalyst patented by Estman Company and based on Ir and a La promoter the catalyst is a molecular species with distinct sites formed from two metal atoms on an activated carbon support. The Ir-La/C catalyst showed comparable reactivity and selectivity to the analogous homogeneous system. It has been shown from mechanistic studies that the most likely carbonylation mechanism over the Ir-La/C catalyst involves the La promoting CO insertion by abstracting an iodine from the active Ir center. The use of La as promoter instead of Ru can contribute to reduce the cost of the catalyst. It was recently shown that the introduction of sulfonic acidic groups into the Ir-La/C catalyst promotes the carbonylation by maintaining an atomic dispersion of Ir on the support.¹⁹² Interestingly, gold catalyst on carbon were demonstrated to be as least as active as the iridium systems.¹⁰⁷

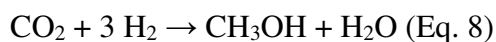
8. Carbonylation with carbon dioxide as CO surrogate

The carbonylation reaction can be performed with a 70 % yield based on methanol using the couple CO_2/H_2 .^{193,194} The catalytic reaction needs the two precursors $[\text{Ru}_3(\text{CO})_{12}]/[\text{Rh}_2(\text{OCOCH}_3)_4]$ with the imidazole ligand in the presence of LiI at 200 °C and 80 bar in 1,3-dimethyl-2-imidazolidinone as solvent. Five catalytic runs lead to around the same reactivity and the turnover number reaches 1000. With this system, the alcohols formation is negligible. CH_3I formed by reaction of LiI on methanol produces the oxidative addition on the Rh species: after coordination of CO_2 the migratory methyl reaction generates a Rh-COOCH₃ bond which is hydrogenated into CH_3COOH by the ruthenium catalyst.¹⁹³ Evidence of the CO_2 pathway is based on experiments using CH_3OD , $\text{CH}_3^{18}\text{OH}$ and $^{13}\text{CH}_3\text{OH}$. Further studies revealed that the $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]/\text{LiCl}/\text{LiI}/4\text{-methylimidazole}$ system is still more efficient than the Rh/Ru one,¹⁹⁵ since at 180 °C and 50 bar $\text{CO}/50$ bar H_2 , in 1,3-dimethyl-2-imidazolidinone, the yield in acetic acid is 82 % and the turnover frequency 26.2 h⁻¹. Here also, the oxidative addition of CH_3I generates an Rh-CH₃ species and the CO_2 coordination followed with the methyl migratory insertion leads to an Rh-COOCH₃ species. Isotopic studies support a reaction pathway that does not proceed *via* the CO route.

Through an electrocatalytic procedure, it is possible to convert directly carbon dioxide into acetic acid. With copper(I) complexes containing the *N,N,N',N'*-tetra(2-pyridyl)-2,6-pyridine-diamine and *N,N,N',N'*-tetra(2-pyridyl)-biphenyl-4,4'-diamine ligands supported on carbon doped boron nitride, in 1-ethyl-3-methyl-imidazolium tetrafluoroborate/LiI/water solution the Faradic efficiency can reach 80 %.¹⁹⁶

Interestingly, two efficient catalysts formed of MnO_x particles supported on mesoporous Co_3O_4 or one Cu-nanocrystal encapsulated within a single Zr(IV)-based Metal-Organic Framework have been reported to promote a cobalt catalyst hydrogenation of CO_2 that gives

rise to methanol with a 100 % selectivity (200 °C, 10 bar). It is thus possible to synthesize acetic acid exclusively from carbon dioxide.¹⁹⁷



The *George Olah Plant* is today operating with copper-zinc oxide-alumina to produce about 5000 T.y⁻¹ of methanol in Iceland and the size of the plant could reach 35 000 T.y⁻¹ in a few years.¹⁹⁸

Finally, mixtures of formic and acetic acids were produced under relatively mild conditions (35 bar and 130 °C) by CO₂ hydrogenation on Ni/Al₂O₃ catalysts.¹⁹⁹

9. Conclusions

Methanol carbonylation is one of the oldest reaction of homogeneous catalysis that was developed industrially, mainly because of stability issues associated with the heterogeneous systems. Today, even if plants of capacities as large as 1 500 000 T.y⁻¹ are still built using the *historical* homogeneous rhodium or iridium catalysts, efforts are still devoted to improve these catalysts, in particular by addition of ligands, which could increase their activity. Although it has been clearly shown that ligand addition, can indeed results in higher reaction rate, up to date stability issues often limit this strategy. In that context, catalytic studies including multiple recycling or long-term continuous operations should be encouraged. More studies based on the improvement of catalyst stability as well as their promotion should also be conducted. The immobilization of these homogeneous systems, as in the case of the AceticaTM process is also an interesting option from the catalyst separation point of view in new units. There also, catalyst stability should be carefully examined.

In parallel, several heterogeneous systems are still today under investigation, with a specific focus on developing catalysts based on abundant and low price metals, and avoiding iodide promoters. In that context, many studies have shown that using montmorillonites, mordenites or zeolites as catalyst or catalyst supports allows one reaching relatively high productivities and selectivities in acetic acid. However, in order the heterogeneous catalysts can operate under long time reaction rates, they have still to be significantly improved in a next future, in terms of both activity and selectivity but also stability. The separation of the components would result in lower operation costs. Finally, the use of carbon dioxide not only to carbonylate methanol, but also to produce methanol directly from its hydrogenation is an attractive synthetic way to prepare acetic acid or its derivatives on a modest scale.²⁰⁰ Further studies should be conducted in this direction, both with homogeneous or heterogeneous systems.

10. References

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