New catalyst complexes of acetic acid synthesis from methanol carbonylation reaction: A Review

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Abstract

Acetic acid has been used as a significant reactant in some chemical processes. Furthermore, it is utilized as a solvent for the synthesis of precious components. Methanol Carbonylation is one of the production methods of acetic acid. Methanol carbonylation reaction has been noticeably studied by using homogeneous and heterogeneous catalysts. In addition, some different supporting materials such as carbon active, clay, alumina, silica, zeolite, or other adsorbents have been recently investigated for developing the effective heterogeneous catalysts. For the determination of the effects of liquid-phase catalysts, several commercialized homogeneous catalysts have been reported for the synthesis of acetic acid by methanol carbonylation, which includes, metal-organic complexes such as cobalt, ruthenium, iridium, nickel, or rhodium-based homogeneous catalysts. Although the use of homogeneous rhodium or iridium complexes in the acetic acid industry is high efficiencies, arguably the use of heterogeneous catalysts has preponderance such as easy separation that leads to less catalyst waste. As a result, various materials such as activated carbon, clay, alumina, silica, and zeolite have been survived as a catalytic base for the development of acetic acid heterogeneous catalysts. Moreover, the influences components which have been used for the carbonylation of methanol in the liquid or vapor phase are Zeolite, nickel, copper, gold, platinum, palladium, osmium, copper-nickel, copper-Mordenite, palladium-cerium, ruthenium-rhodium, and lanthanum-rhodium. It is inevitable that, modification of a rhodium-based homogeneous catalyst with the addition of ligands is another way to increase catalytic activity. Phosphine ligands and their derivatives have received more attention in studies. The present paper summarizes commercialized chemical processes with rhodium and iridium-based catalytic systems in a liquid-phase carbonylation reaction such as Monsanto, Cativa, Acetica, as well as a number of alternative catalytic systems including heterogeneous catalysts to solve some process issues such as insufficient separation of homogeneous catalysts from a corrosive liquid-phase reaction medium. It was found that homogeneous complexes containing phosphorus ligands and zeolites as catalyst support are promising systems in the production of acetic acid.

Keywords: Acetic acid, Methanol carbonylation, Monsanto process, Rhodium complexes, Heterogeneous and Homogeneous catalysts

1- Introduction

Acetic acid is one of the most important industrial and commercial chemicals that produced by more than eight million tons per year and has a wide application in the industry. [1]. Acetic acid (AA, CH_3COOH) is widely identical as one of the important chemical intermediate for industrial applications such as raw materials for synthesis of vinyl acetate monomer (VAM), acetate or anhydrate acetate, ester acetate and solvent for pure terephthalic acid synthesis [2]. Acetic acid is also largely used to produce vinegar (approximately 4-8% of acid dilutedin water). The production of acetic acid from 2015 is significantly growing from 13 million tons to 18 million tons in 2020, so annual growth is approximately 5% [3]. More than 65% of acid production in the world are transformed into polymers through the synthesis of Venyl acetate or its monomer production. Most polyvinyl acetate is used for color ingredients and coatings or for the production of polyvinyl alcohol as well as plastics. The development of an efficient catalytic process for producing acetic acid is largely focused on optimizing heterogeneous and homogeneous catalysts for liquid carbonylation reaction [4].

The new processes and catalysts of acetic acid from the 1950s are continuously introduced and improved. The purpose of the development of new acetic acid process was to reduce the consumption of raw materials, energy requirements and investment costs. A significant cost advantage has led to the use of carbon monoxide (derived from natural gas) and cheap methanol (from synthesis gas) as raw materials. Currently, from the industrial processes of AA production, methanol carbonylation is dominant [5].

$$CH_3OH + CO \rightarrow CH_3COOH \tag{1}$$
$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O \tag{2}$$

Methanol carbonylation is characterized by the VIII transition metal complexes, especially by rhodium, iridium, cobalt and nickel catalytic. All methanol carbonyl processes need Iodid compounds as promoters, methyle iodide is a promotor for the reaction, and the intermediate metal involved alkaline. Apart from acetic acid, methanol carbonylation (equation (1)) leads to the formation of methyl acetate in accordance with the equation 2. In some carbonylation processes (cativa), methyl acetate is used as solvent [5].

Different commercialized processes for producing acetic acid, including BASF, Monsanto, Cativa and Acetica processes under the reaction of liquid phase using a homogeneous catalyst based on rhodium and iridium, however, there are many problems that should be solved, such as difficult separation homogeneous catalysts from corrosive liquid phase reaction and easy formation of metal salts and so on. Therefore, several processes such as direct vapor-phase or indirect phase to reduce the problems of liquid phase through direct oxidation of hydrocarbons or multi-stage reactions through the synthesis of dimethyl ether or methyl acetate intermediates are known as the BP-SaaBre process. In terms of economic feasibility, the commercial processes of acetic acid production from different raw materials, the Monsanto and Cativa process for liquid carbonylation reaction compared to direct oxidation of hydrocarbons have been the most effective processes. The present paper presents a summary of the commercial processes of liquid phase with their catalytic system as well as analyzing some new catalytic systems for methanol carbonation reaction using homogeneous and heterogeneous catalysts.

2. Industrial methanol-to-acetic acid processes

The methanol carbonylation of the liquid phase to AA is performed using methanol and the additional amount of carbon monoxide, equilibrium conversion can be increased by increasing the reaction pressure and reaction temperature in the opposite direction through the following reactions.

$$CH_3OH + CO \rightarrow CH_3COOH \tag{3}$$
$$CH_3OH + HI \rightarrow CH_3I + H_2O \tag{4}$$
$$CH_3I + CO \rightarrow CH_3COOI \tag{5}$$
$$CH_3COOH + H_2O \rightarrow CH_3COOH + HI \tag{6}$$

Several commercial homogeneous catalysts for synthesis of acetic acid by liquid methanol carbonylation have been reported by metal-organic complexes such as cobalt, rotenium, iridium, nickel or homogeneous catalysts are based on rhodium. Since the mid-1960s, the methanol carbonyl reaction of liquid phase with homogeneous catalysts based on cobalt or rhodium under the BASF license (cobalt-based catalyst) and Monsanto (rhodium-based catalyst). In addition, the presence of halogenative promoters such as methyl iodide or iodide acid, for liquid phase carbonylation of active metal complexes through the mechanism of oxidation-reduction compounds, are inevitable. The role of halogenal additives is to activate C-O bond in methanol molecules on trantion metal complexes. In order to insert carbon monoxide to C-O methanol, a reactive molecule, such as promoter iodide, is usually required to convert methanol by reaction 4 to methyl iodide. Methyl iodide formed through equation 4 reacts with carbon monoxide and acetyl-iodide forms, which can quickly reach acetic acid final product through 6 reactions. [6].

Many chemical companies such as BASF, Monsanto, BP, Chiyoda, Celanese, and other manufacturers have their own patents to produce AA with a yield over 99 % using different homogeneous Co, Rh, or Ir-based metal–organic complexes or heterogenized homogeneous Rh-based catalyst. The comparisons between the commercialized processes for AA production in liquid-phases are summarized in Table 1. These commercialized processes for AA production by methanol carbonylation in a liquid phase such as BASF, Monsanto, Celanese, Cativa, and Acetica process, were schematically represented in Fig. 1. These commercial processes are mainly composed of three units such as a liquid-phase slurry reactor, catalyst separation by flash separation tank, and two or three separation columns like drying and heavy end column[7].

Table 1.Commercialized processes for liquid-phase methanol carbonylation to AA

Commercialized liquid-phase process for AA synthesis					
	BASF	Monsanto	Cativa	Modified Cativa	Chiyoda-UOP (Acetica)
Catalysts type (metal–organic complex)	Cobalt/MeI	Rhodium/ MeI	Iridium/iodide	Iridium/MeI	Heterogenized rhodium
Co-catalyst (promoter)	-	-	CH_3I, H_2	$[Ru(CO)_xI_y]$	-
Temperature (℃)	230	150-200	190	190	160-200
Pressure (MPa)	6.0-8.0	3.0-6.0	2.8	2.8	3.0-6.0
Yield (methanol based, %)	90	99	>99	>99	99
Main byproducts	Methane, acetaldehyde, ethanol and ethers	Not reported	Not reported	Not reported	Ester, ether and water

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Nevertheless, the main problem of these homogeneous catalytic systems is the difficult separation of expensive metal complexes of the homogeneous corrosive products, which generally contain some metal salts with CH_3I reactor and also the HI side product [5]. In the following sections, some commercialized processes for the synthesis of acetic acid from liquid phase carbonylation based on the mechanism of homogeneous catalytic reaction with their properties are described.
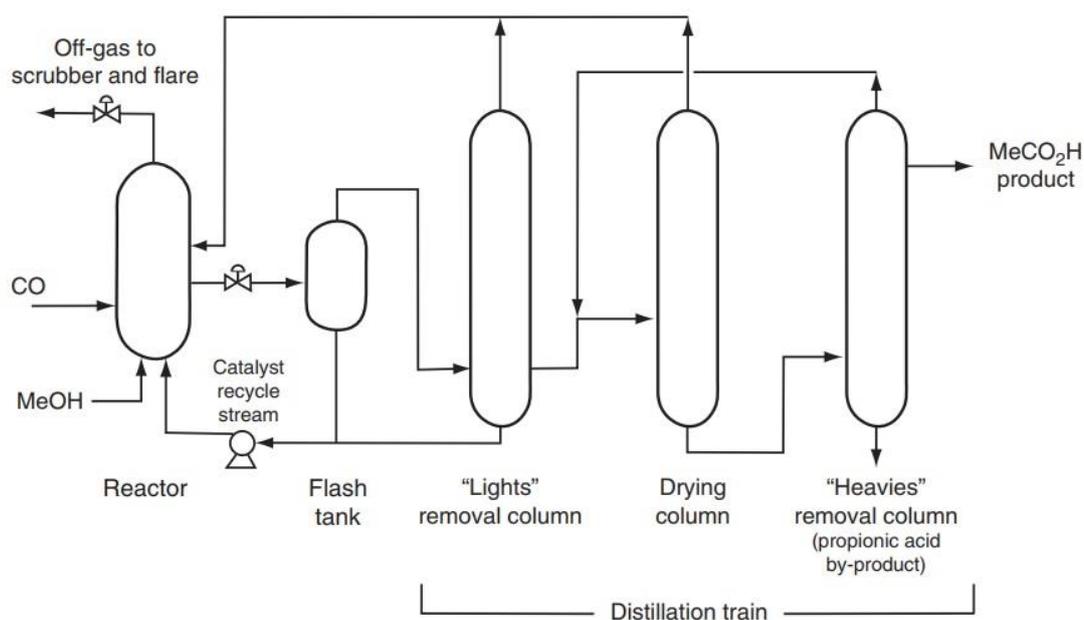
Fig. 1 . General commercialized process schemes for AA synthesis by methanol carbonylation in a liquid-phase

2.1 BASF Process with Homogeneous Co-Based Catalyst

The first commercial acetic acid production process, liquid phase methanol carbonylation using a homogeneous catalyst, was the BASF process in the early 1960s. The BASF process was performed using a cobalt-based homogeneous catalyst and an iodide promoter, at pressures above 6.0-8.0 MPa and temperatures above 230°C. 0.1 M Cobalt based homogeneous catalyst was used and the yield of acetic acid was 70% based on CO reactant and 90% based on methanol reactant [1]. By-products such as methane, acetaldehyde, ethanol and ethers were produced in small quantities during the reaction. The proposed reaction mechanism shows that the hydride-cobalt carbonyl group $HCo(CO)_4$ is an active site for carbonylation with the help of CH_3I promoter and water enhances CH_3COI mediator formation, as shown in Figure 2.

In the BASF process, the presence of iodide is necessary to convert methanol to methyl iodide before methanol carbonylation, because highly active methyl iodide can effectively activate methanol for carbonylation. Thus iodide species play an important role in breaking down alkyl intermediate through the formation of acetyl iodide intermediate. In the absence of an iodide promoter, the CO molecule prefers to enter the O-H methanol bond to form methyl formate instead of entering the C-O methanol bond to form acetic acid. Although the BASF process requires relatively high pressures and temperatures, it has been reported that operating pressures can be significantly reduced by modifying the cobalt-based complex with Ru, Ir, Pd, Pt or Cu promoters [7].
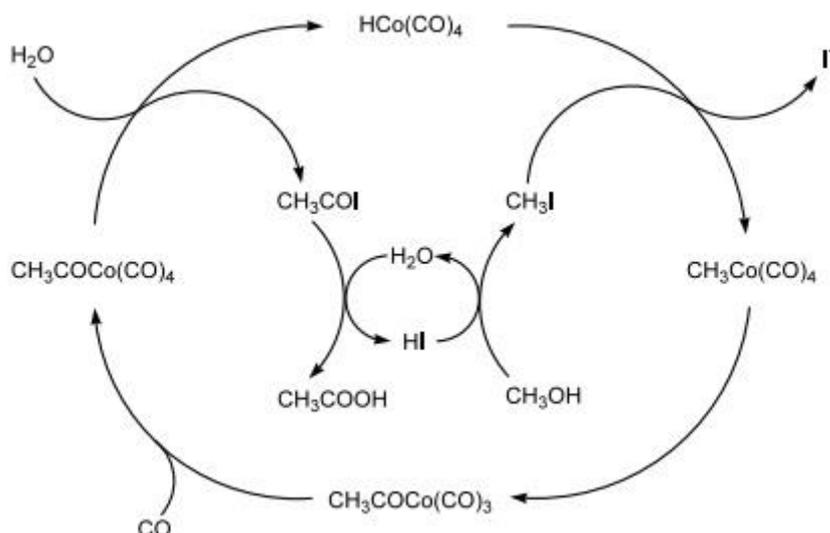
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Fig. 2. Catalytic cycle of the cobalt-catalyzed methanol carbonylation (BASF process)

2.2 Monsanto Process with Homogeneous Rh-Based Catalyst

The Monsanto process was commercialized in 1966 using an improved Rh-based homogeneous catalyst for the liquid phase methanol carbonylation with methyl iodide, which had a relatively lower pressure and temperature than the BASF process. The Monsanto process operates in the pressure range of 3-6 MPa and in the temperature range of 150-200 °C, where the reaction conditions are more moderate than the BASF process. Acetic acid selectivity based on methanol reactant has been reported to be about 99%. [8]. The mechanism of the catalytic reaction on the homogeneous methyl-iodide promoted rhodium catalyst was presented by the Monsanto process with 6 main cyclic steps through the formation of 4 different intermediates which are shown in Figure 3.

Step 1 Methanol can be initially reacted with iodide species to form methyl iodide (CH_3I) intermediate and water as well; Step 2 Anionic species of cis-$[Rh(CO)_2I_2]^-$ (A) can be formed as an initial active species, and it interacts with a substrate of CH_3I which can be formed from Step 1 between methanol and iodide acid. Through Step 2, the hexacoordinated complex of $[(CH_3)Rh(CO)_2-I_3]^-$ (B) can be formed which is kinetically unstable species. Step 3 Formed $[(CH_3)Rh(CO)_2I_3]$ (B) species can be further transformed into an isomeric pentacoordinated acetyl complex $[(CH_3CO)-Rh(CO)I_3]$- (C), which can be resulted from a migration of methyl group to CO ligands. Step 4 The complex (C) reacts rapidly with CO to form the six-coordinated dicarbonyl complex $[(CH_3CO)^- Rh(CO)_2I_3]^-$ (D) by forming a terminal CO group. Step 5 Six-coordinated dicarbonyl complex (D) eliminates CH_3-COI intermediate and then it can be regenerated to an original rhodium complex $[Rh(CO)_2I_2]$- (A). The regenerated rhodium complex (A) can initiate next catalytic cycle as well. Step 6 Finally, a final product of AA can be formed from a hydrolysis of acetyl iodide with water, which has been known to be very rapid in the presence of excess water [9].
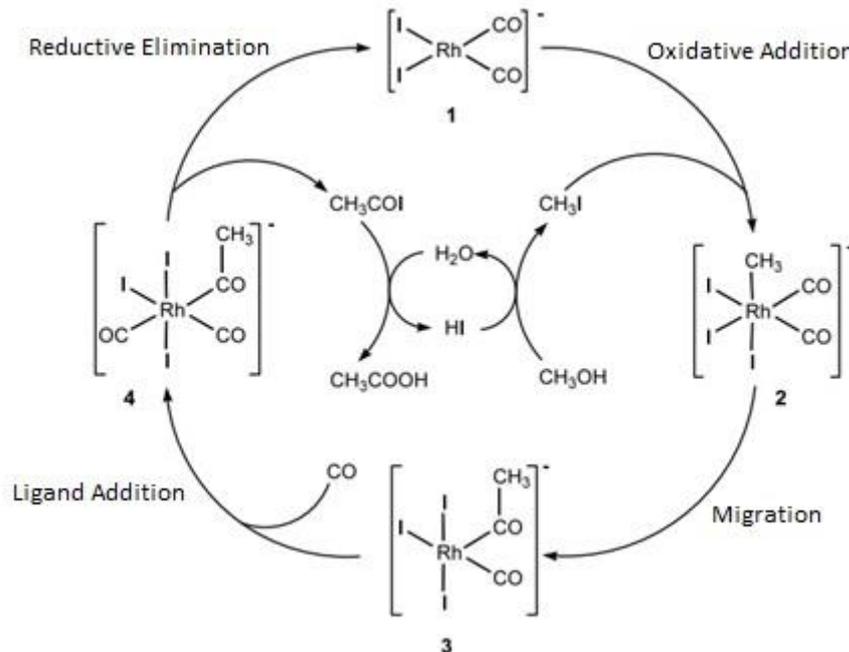
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Fig. 3. Catalytic cycle of the rhodium-catalyzed methanol carbonylation (Monsanto process).

The reaction rate on methyl iodide-promoted rhodium complexes is independent of the concentration of methanol and carbon monoxide. The addition of methyl iodide oxidizer to the center of the rhodium complex (A) in step 2 can also be suggested as a rate-determining step for methanol carbonylation. In addition, the reaction rate with respect to methanol and methyl iodide appears to be the first reaction under normal reaction conditions. Therefore, an adequate amount of excess water (14-15% by weight) is essentially required to achieve high catalytic activity and maintain the stability of the Rh-based homogeneous catalyst. Otherwise, less water will change the rate-determining step to reductive elimination of acetyl species through step 5 by changing the product distribution. Although water appears to be essential in the liquid-phase methanol carbonylation, excess water tends to form CO_2 by the water-gas transfer reaction (WGS), which generally competes with the methanol carbonylation reaction, as shown in Figure 4[9]. Even though water seems to be necessary in a liquid-phase methanol carbonylation, the excess amount of water also tends to form CO_2 by water–gas shift (WGS) reaction, which generally competes with methanol carbonylation reaction as illustrated in Fig.4.

Therefore, methanol carbonylation on the active rhodium-based anion $[Rh(CO)_2I_2]^-$ catalyst with HI promoter can enhance the formation rate of $[Rh(CO)_2I_3H]^-$ preferentially. The unstable intermediate of $[Rh(CO)_2I_3H]^-$ can further react with another HI by releasing H_2 and form tetra iodide complex of $[Rh(CO)_2I_4]^-$. Therefore, an increase of water concentration in reaction medium can accelerate the formation rate of $[Rh(CO)_2I_4]^-$ intermediate to form its counterpart basic species such as $[Rh(CO)_2I_2]^-$. These cyclic mechanisms strongly suggest that a proper amount of water can help both to keep rhodium-complex stable in its original active sites and to prevent precipitation of inactive rhodium salts and so on [5].
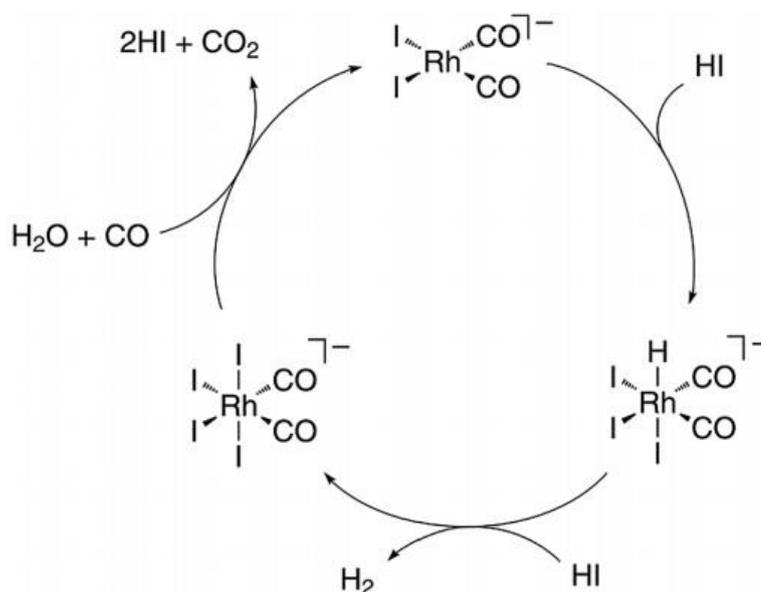
Fig. 4. Catalytic cycle of the water/gas shift reaction as side reaction in the rhodium-catalyzed methanol carbonylation.

2.3 Celanese Process with Homogeneous Rh-Based Catalyst

Hoechest-Celanese Process the commercial process of acetic acid production by liquid phase methanol carbonylation using a homogeneous Rh-based catalyst with a lithium iodide (LiI) promoter to activate operations at low concentrations of iodide and water was recorded in 1986 [6]. Due to the low water concentration, WGS activity can be minimized by decreasing the mediator concentration of $[Rh(CO)_2I_2]$ - as shown in Figure 3. Due to the possible reaction of methyl acetate with the LiI promoter, as shown in Equation 7 and then Equation 8, it is possible to apply high concentrations of methyl acetate to the Celanese process.

$$CH_3COOCH_3 + LiI \rightarrow MeI + CH_3COOLi \tag{7}$$

$$CH_3COOLi + \rightarrow LiI + CH_3COOH \tag{8}$$

In summary, a higher concentration of methyl acetate intermediate seems to be resulted in a lower HI concentration, which tends to suppress an oxidation of $[Rh(CO)_2I_2]$ intermediate to form $[Rh(CO)_2I_4]^-$. These positive effects of lithium iodide promoter can suppress the activity of WGS reaction, which is significantly beneficial for a long-term catalyst stability under the carbonylation reaction conditions [8]. Evidence has been presented that iodide salts can promote the oxidative addition of MeI to $[Rh(CO)_2I_2]^-$, the rate-determining step in the Rh cycle. Iodide salts have also been found to be effective promoters for the anhydrous carbonylation of methyl acetate to acetic anhydride. In the absence of water, the catalyst cannot be maintained in its active form ($[Rh(CO)_2I_2]^-$) by addition of LiI alone, and some H_2 is added to the gas feed to reduce the inactive $[Rh(CO)_2I_4]^-$ [10].

2.4 Cativa Process with Homogeneous Ir-Based Catalyst

Cativa[TM] process was first announced by BP Chemicals in 1996 using a homogeneous Iridium-based Ir catalyst. The Cativa process significantly improved compared to the Monsanto process (Rd-based complex), including improved catalyst stability, high activity even at low water concentrations, and reduced by-product formation. [11]. The Cativa process is also known as a greener and more efficient process than the Monsanto process. Water and electricity consumption and factory construction costs can be reduced by up to 30%, as Cativa process designs are simplified and by-product formation is reduced. For example, the treatment phase can be simplified due to intensive operating conditions with lower water concentration and less by-product formation, which can reduce reactor size and operating costs compared to the Monsanto process [12]. As shown in Fig. 5, the reaction mechanisms of anionic iridium complexes are similar with rhodium-based homogeneous catalysts such as Monsanto and Celanese process. However, an oxidative addition rate of methyl iodide to an iridium complex can be increased up to 150 times faster than the rhodium-based homogeneous catalysts [11].
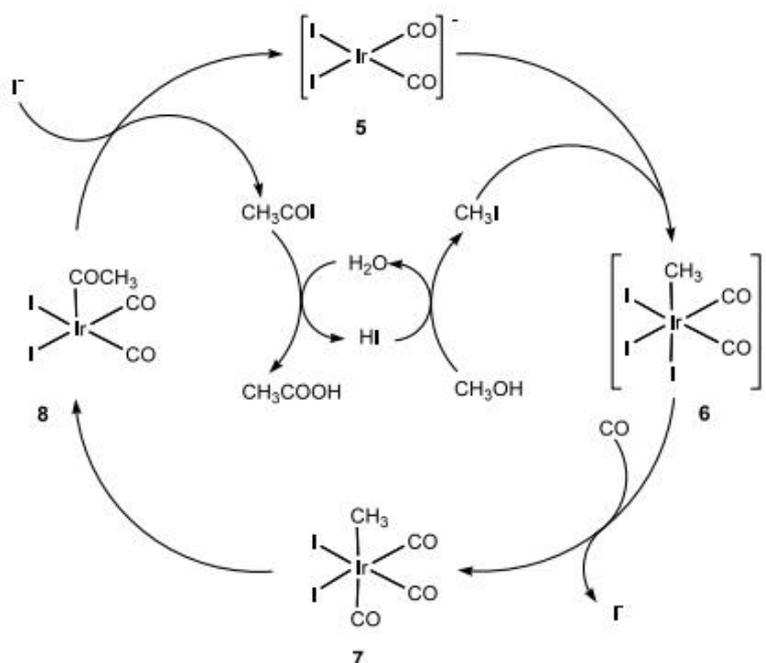

Fig. 5. Catalytic cycle of the iridium-catalyzed methanol carbonylation (Cativa process).

An oxidative addition of methyl iodide to iridium complex was reported not to be a rate determining step even though this step was a rate determining step on the rhodium-based catalyst. The rate determining step of iridium-based Cativa catalyst was proposed as an insertion of CO molecule to an iridium-acyl species through an elimination of ionic iodide from the iridium complex intermediate as summarized in Fig. 5. In order to improve the activity of iridium-based homogeneous catalysts, various types of metal promoters were investigated; metal promoters can reduce the concentration of I^-, which can help iodide consumption during the catalytic cycle. For example, the

addition of a retnium promoter with a molar ratio of 1 to 5 retnium to iridium can improve the catalytic activity of an Ir-based catalyst by almost three times the activity of a rhodium-based catalyst. Based on the iridium-based homogeneous catalyst with retnium promoter, the Cativa process was successfully commercialized in 1995 by BP Chemicals [11].

2.5 Chiyoda/UOP Acetica Process with Heterogenized Homogeneous Rh-Based Catalyst

Chiyoda/Universal Oil Products (UOP) process has been firstly commercialized using a heterogenized homogeneous rhodium based catalyst. The most important progress of the Chiyoda/UOP process seems to be the usage of the immobilized rhodium complex on novel polymer resins firstly. The heterogenized homogeneous catalyst showed a high activity, long-term stability, and no significant rhodium loss in a liquid-phase carbonylation reaction [13]. The process developed by Chiyoda in conjunction with UOP was called the Acetica^{TM} process, and its homogeneous-heterogeneous catalyst was a rhodium complex based on polyvinyl pyridine resin (PVP). Acetica catalyst is able to withstand high temperatures and pressures. Therefore, with effective limitation on PVP resin, the loss of the expensive rhodium metal complex is negligible [14]. PVP resin has terminal nitrogen atoms that are positively charged after forming a quaternization bond with a methyl iodide promoter. In addition, the active sites of rhodium can be converted to the active catalytic anion $[Rh(CO)_2I_2]$ - which is incorporated into the polymer matrix by strong electrostatic interaction with the PVP resin, as shown in Figure 6. Thus, the active anionic rhodium complex in the form of $[Rh(CO)_2I_2]^2$ can be stabilized on a positively charged polymer matrix after cross-ion exchange. [15].
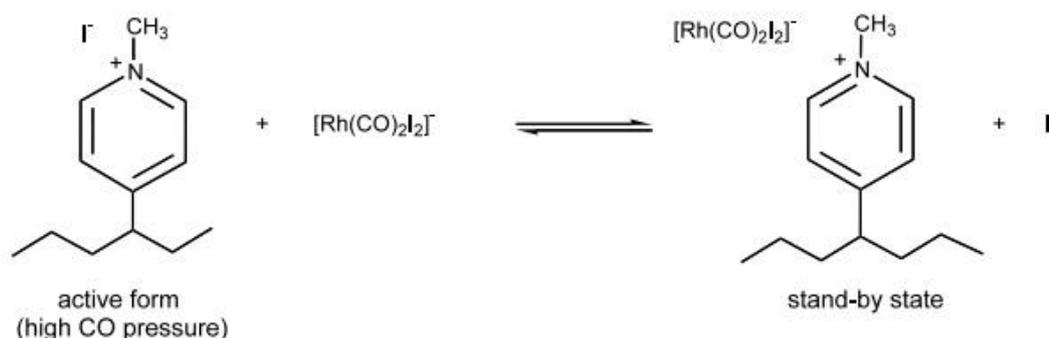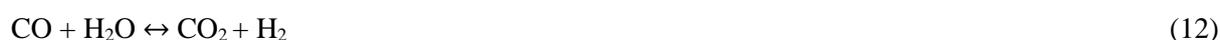

Fig. 6. Proposed mechanisms of rhodium complex fixation on the PVP resin used in the Acetica process

In the Acetica process, methanol carbonylation is performed under temperature conditions of 160-200℃ and pressures of 3.0-6.0 MPa. During the reaction, by-products such as methyl acetate and dimethyl ether are mainly produced by the possible esterification reaction of acetic acid with methanol during reaction equation 9 and the dehydrogenation of two methanol molecules during reaction equation 10, respectively. About 3-8% of water can also be produced during these two side reactions, which can react with the methyl iodide promoter forward to form HI and water for the water-to-gas conversion reaction in reaction equations 11 and 12. In addition, possible reactions of

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methanol reduction to methane have been reported during Reaction 13. Side reactions such as WGS and methanol reduction can occur on rhodium-based homogeneous-heterogeneous catalysts; however, a loss of CO and methanol through the side reactions have been generally known to be less than 1% [15].

$$CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3 + H_2O \qquad (9)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (10)$$

$$CH_3I + H_2O \rightarrow CH_3OH + HI \qquad (11)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (12)$$

$$CH_3OH + H_2 \leftrightarrow CH_4 + H_2O \qquad (13)$$

It has been reported that acetica-based rhodium-based homogeneous-heterogeneous catalysts are slightly inactivated even after continuous operation for more than 7000 hours with slight leaching problems due to stabilization of the active complex on PVP resin. Since the amount of water in the Acetica process is about 3-8%, it is significantly less than the rhodium-based homogeneous catalyst by about 15%. Minor CO_2, H_2 and CH_4 emissions of less than 1% can also be an advantage of the Acetica process. HI production can also be reduced by lowering CH_3I with water due to lower water concentrations, which in turn can prevent corrosion [15].

3- Catalyst Development for Methanol Carbonylation Reaction

Acetic acid synthesis by methanol carbonylation using Rh or Ir-based homogeneous and heterogeneous catalysts through Monsanto, Cativa and Acetica processes was introduced in the previous section. However, the difficult process of separating precious metal complexes from corrosive products in the above commercial processes , Generally increases the cost of the product. Therefore, many efforts have been made to improve efficient heterogeneous catalytic systems with high acetic acid productivity under milder operating conditions. The development of some new heterogeneous catalytic systems using completely heterogeneous catalysts operating under the liquid phase or vapor phase reaction has been very attractive for the easy separation of the catalyst from the liquid reaction medium containing acidic products. Some attempts to develop heterogeneous catalysts for the vapor phase carbonization reaction have also been extensively reviewed to facilitate catalyst and product recovery. Recently, various materials such as activated carbon, clay, alumina, silica, zeolite or other adsorbents have been used to develop heterogeneous catalysts. In the next section, we review some research on the development of homogeneous and heterogeneous catalysts for liquid phase methanol carbonylation.

3.1 Alternative Nickel-Based Homogeneous Catalysts

A homogeneous catalyst to replace commercially available catalysts is a nickel-based catalyst, which is attractive because of its low cost compared to rhodium or iridium-based catalysts. The active species of nickel-based homogeneous catalysts are carbonyl-nickel species, which can be produced in the presence of iodine during the following reaction:

$$NiI_2 + H_2O + 5CO \rightarrow Ni(CO)_4 + 2HI + CO_2 \qquad (13)$$

The active species is carbonyl-nickel, and the reaction process on homogeneous nickel complexes is similar to commercial rhodium-based Monsanto catalysts. The proposed possible reaction mechanism of methanol carbonylation on a nickel-based homogeneous catalyst is schematically shown in Figure 7 [16]. Initially, the iodide acid species formed reacts with methanol through a cyclic mechanism to convert to alkyl halide (CH_3I), then by adding CH_3I to $Ni(CO)_4$, acetyl-nickel iodide $Ni(CO)_2$ (CH_3I) is generated. Addition of another CO molecule to $Ni(CO)_2$ (CH_3I) can form $Ni(CO)_2COCH_3I$). Upon entry of two CO molecules into the complex, the active species $Ni(CO)_4$ is reproduced by the release of acetyl iodide (CH_3COI). Subsequently, the intermediate of acetyl iodide can be hydrolyzed by water or alcohol to form acetic acid [17].
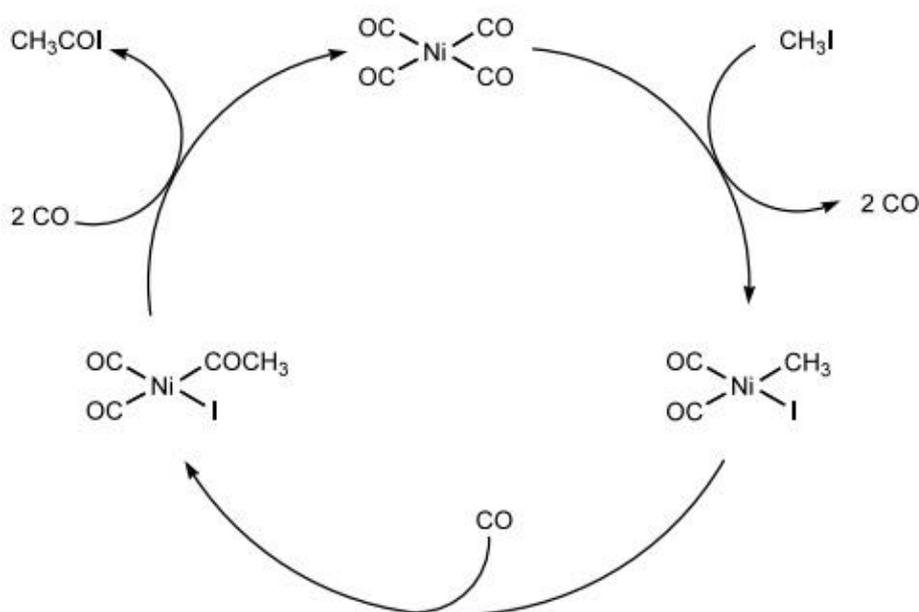

Fig. 7. Catalytic cycle of the nickel-catalyzed methanol carbonylation

Nickel-based homogeneous catalysts are easily stable even at lower water concentrations compared to the Monsanto process, and this process is more economically feasible than rhodium complexes due to the use of a cheaper nickel complex. In the case of a nickel-based homogeneous catalyst, the reaction still requires a relatively high pressure and temperature to obtain reasonable catalytic activity. However, higher concentrations of the iodide precursor can optimize the reaction temperature and pressure. The modified nickel-based homogeneous catalyst can be an alternative catalytic system to meet the same catalytic performance compared to rhodium-based homogeneous catalysts [16]. Unfortunately, although the nickel complex seems to be much cheaper than rhodium-based complexes, no commercialized processes have been reported so far due to problems such as $Ni(CO)_4$ intermediate toxicity and lower AA yields.

3-1-1. Nickel-based heterogeneous catalysts in the vapor phase

Nickel-based heterogeneous catalysts for the carbonation of methanol in the vapor phase for the production of methyl acetate and acetic acid have been investigated [18, 19]. Nickel-based heterogeneous catalysts deposited on various supports such as gamma alumina, silica and other

materials such as activated carbon, graphite and carbon black under reaction conditions of 300 °C and 1.1 MPa in vapor phase in the presence of methyl promoter Iodide was examined [18, 20]. Nickel-based heterogeneous catalysts deposited on different supports showed lower acetic acid yields than nickel based on activated carbon. The pore size distribution and the average pore diameter of carbon bases have a significant effect. Deactivation of nickel-based heterogeneous catalysts is associated with stronger adsorption properties than methanol and related products, which can block the catalyst pores and gradually prevent the penetration of the reactants over time [18].

Carbonation of methanol vapor phase with carbon monoxide using Ni/AC catalyst has been studied for many years. Compared to the traditional homogeneous carbonation process, it has the advantages of low cost and easy separation. However, the Ni/AC catalyst is not stable enough for industrial use and its deactivation mechanism is still under investigation.

Fei Pang et al. [21] investigated the effects of oxygen-containing groups on the activity and stability of Ni/AC catalysts. Activated carbon with different concentrations of HNO_3 solution for the preparation of Ni/AC catalysts with different amounts of oxygen. Surface deposition of carbon and accumulation of nickel particles reduced the reactivity of the catalyst, which could be regenerated by operation under hydrogen at 400 °C. It was found that catalysts with lower oxygen-containing groups showed higher initial activity and higher inactivation rate, which was consistent with the density rate of oxygen-containing groups. The high oxygen content prevents the accumulation of oxygen-containing carbon deposits and thus provides better catalytic stability for carbonylation.

3-2. Alternative rhodium-based homogeneous catalyst

The migratory insertion reaction of CO into metal/alkyl bonds is a fundamental step in the metal iodide catalyzed carbonylation of methanol to acetic acid. The conditions used industrially (30-60 bar pressure and 150-200℃) with the original $[Rh(CO)_2I_2]^-$ catalyst have spurred the search for new catalysts, which could work in milder conditions. The rate determining step of the rhodium-based catalytic cycle is the oxidative addition of CH_3I, so that catalyst design focused on the improvement of this reaction. The basic idea was that ligands which increase the electron density at the metal should promote oxidative addition, and consequently increase the overall rate of the reaction. For this purpose, other rhodium complexes have been synthesized in the last years, and they have been shown to be active catalysts of comparable or better performance as compared to the Monsanto catalyst [22]. Although rhodium homogeneous catalysts result in a high selectivity of 99% relative to acetic acid and a significant conversion number, many studies have been performed to further improve the reaction rate by replacing the CO ligand with a more nuclear core ligand to accelerate the addition of CH_3I oxidative species [22]. Phosphine ligand is preferred in most of these studies because phosphorous ligands have the ability to change the properties of intermediate metals with a lower oxidation state, as well as the flexibility of the combined phosphor atoms, known in the field of coordination chemistry [23].

In addition, some ligands, including nitrogen atoms, have been attractive for the production of rhodium-based homogeneous catalysts due to the easy adaptation of the binding energy to both high and low oxidation states. Unlike the phosphorus atom, the nitrogen atom has only the σ-donor property (without π acceptor) which can produce more ionic properties in the ligand bonds of the intermediate metal than the phosphorus atom. Thus, a nitrogen-containing metal ligand with a strong σ-donor capability can enhance the nucleophilicity of the rhodium center, which in turn increases the catalytic activity of the rhodium complex in the carbonylation of methanol to acetic acid. Based

on these properties, study of rhodium complexes containing pyridine (Py) species such as Py-2-COOH, Py-3-COOH, Py-4-COOH ligands and different types of benzyl pyridine ligands to determine the effect of ligand on carbonylation liquid phase of methanol to acetic acid has been extensively investigated [23, 24]. Using modified rhodium-based homogeneous catalysts, reasonable catalytic performance was observed as summarized in Table 2 [25].

The possible reaction mechanism proposed for the carbonylation of methanol to acetic acid in the presence of ligand precursors in rhodium metal complexes such as Py-2-COOH and Py-3COOH is schematically shown in Figure 8. The details of the mechanism of methanol carbonylation using a homogeneous rhodium complex include the pyridine ligand similar to the mechanism described for the commercial homogeneous rhodium catalyst in the previous section.

Table 2. Some proposed homogeneous catalytic systems for methanol carbonylation to AA in a liquid-phase

Catalysts types	Temperature (°C)	Pressure (bar)	Yield of AA (%) based on methanol
$[Rh(CO)_2Cl(L)]^a$	130	30	32.3
$[Rh(CO)_2Cl(L)]^b$	130	30	58.8
$[Rh(CO)_2Cl(L)]^c$	130	30	46.3
$[Rh(CO)_2Cl(L)]^d$	130	30	6.2
$[Rh(CO)_2Cl(L)]^e$	130	35	9.4
$[Rh(CO)_2Cl(L)]^f$	130	35	6.6

L represents the types of ligands such as: a 2-Benzoylpyridine, b 3-Benzoylpyridine, c 4-Benzoylpyridine, d Py-2-COOH, e Py-3-COOH, f Py-4-COOH
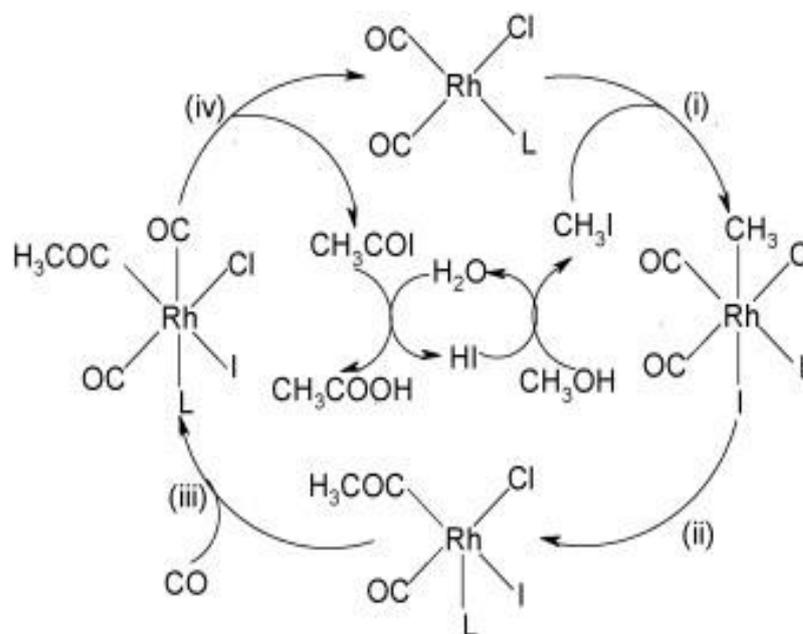

Fig. 8. Proposed catalytic cycles for methanol carbonylation with rhodium complexes containing pyridine carboxylic ligands

The carbonylation of methanol using a catalyst containing triethyl phosphine ligand [RhI(CO)(PEt$_3$)$_2$] has been investigated by John Rankin et al. Their results showed that under operating conditions of temperature 120-150°C and pressure 27 bar, neutral rhodium complex containing triethylphosphine [RhI(CO)(PEt$_3$)$_2$], for carbonylation of methanol to ethanoic acid from [Rh(CO)$_2$I$_2$]$^-$ is more active. For the neutral triethylphosphine complex (PEt$_3$), the CH$_3$I step is 57 times faster at 25 °C while the transfer CO transfer is 38 times slower [26].

3-3. Alternative Rhodium-based Heterogeneous Catalyst

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. 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).

Ji Su Nam et al. [27] prepared a graphite carbon nitride combined with rhodium (Rh-g-C$_3$N$_4$) for carbonylation of the liquid phase of methanol to acetic acid (AA) to overcome the disadvantages of commercial Rh-based homogeneous catalysts. Rh-g-C$_3$N$_4$ heterogeneous catalyst showed significant catalytic activity in liquid phase carbonylation with acetic acid efficiency higher than 82% under 413K reaction conditions and 4.0 MPa CO pressure, which can produce an intermediate (methyl acetate). That easily hydrolyzed to acetic acid. The dispersion of the rhodium nanoparticles contained in the g-C$_3$N$_4$ matrix was responsible for the higher catalytic activity with a lower degree of leaching of rhodium metals. Beyond the acetica^{TM} process polyvinyl pyridine resins, the polymerization of tris (styryl) phosphine results in a solid containing phosphine ligands called POL-PPh$_3$. Rh-POL-PPh$_3$ catalyst was used for methanol carbonylation in a continuous bed reactor with higher activity than [RhI$_2$(CO)$_2$] at 195 °C and 25 bar (TOF = 1550 h^{-1}) with almost stable activity shown for 180 hours. Therefore, POL-PPh$_3$ not only acts as a stable base, but also promotes the methanol carbonylation process [28].

Shasha Zhang et al. [29] designed and synthesized an Rh(I)/Ru(III) catalyst with a bimetallic spatial structure. The interaction between the bimetallic catalyst metals and the attached dimer structure can effectively reduce the spatial barrier effect, increase the reaction rate, and stabilize the catalyst. The results of methanol carbonylation using Rh/Ru catalyst showed that the conversion rate of methyl acetate and acetic acid yield under certain conditions is 96%.

3-4. 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. Because some halide compounds, which are generally used more in the liquid phase of the methanol carbonylation reaction, are highly corrosive to the slurry reactor. Therefore, the use of halide-free heterogeneous catalysts to reduce corrosion problems has been investigated. Several attempts have been made to develop heterogeneous halide-free catalysts using zeolite materials such as Y, copper combined with HZSM-5, and some heteropolyacid catalysts containing active metals such as rhodium or iridium tungstophosphoric [30]. However, none of these heterogeneous catalysts have been commercialized due to their low economic feasibility with poor acetic acid yield and high hydrocarbon formation under the vapor phase carbonization reaction conditions. For example, a

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halide-free heterogeneous catalyst containing an active molecular compound combined with copper such as zeolite mordenite (Cu-MOR) was investigated by BP chemicals, which showed an effective catalytic system for the direct synthesis of AA by methanol carbonylation in the vapor phase. Although methanol conversion was more than 90% for 25 hours, acetyl compounds such as methyl acetate and acetic acid were observed only after 6 hours of reaction [30].

Youming Ni and colleagues synthesized a highly stable, selective, halide-free, and noble metal pyridine-modified H-mordenite zeolite catalyst for the direct carbonylation of methanol to acetic acid. This catalyst can effectively solve the incompatibility of lower carbonization rates at low temperatures (due to inhibition of adsorbed water) and inactivation of the catalyst (due to higher rate of coke formation) at high reaction temperatures. Methanol conversion, acetic acid selectivity can reach about 100%, 95% at 543K, respectively. During the 145-h reaction, only slight inactivation was observed in selectivity above 90% acetic acid and about 98% of steel products. This green process for the production of acetic acid through the direct carbonylation of methanol on the pyridine mordenite Py-MOR catalyst is promising for industrial applications [31].

3-5.Catalysis with copper and gold

Feng Peng et.al developed a series of metallic carbon-based catalysts based on activated carbon. Impregnation of activated carbon with $CuCl_2.2H_2O$ resulted in a $CuCl_2$/AC catalyst with a specific surface area of $1000m^2.g^{-1}$ and a particle size of 20-40 mesh. The results showed that $NiCl_2$/AC has a high conversion of methanol and $CuCl_2$/AC has a high selectivity to methyl acetate for carbonate vapor methanol carbonation without adding any promoter to the feed. $NiCl_2$-$CuCl_2$/AC has higher methanol carbonylation activity and selectivity than $NiCl_2$/AC and the yield of methyl acetate increased by 25%. The optimal composition of the composite catalyst is 5% $NiCl_2$ and 15% $CuCl_2$. The new $NiCl_2$-$CuCl_2$/C catalyst had high activity and good stability for methanol vapor phase carbonylation. Under optimal conditions, methanol conversion was 34.5% and carbonylation selectivity was 94.7% mol [32].

Hai Xia Wang et al. [33] performed direct carbonization of vapor phase methanol, without any methyl iodide in the feed, on $NiCl_2$-$CuCl_2$/HMOR catalysts. They concluded that $NiCl_2$-$CuCl_2$/HMOR catalysts show high activity for methanol carbonylation. The optimum composition of the catalyst was 5% by weight $NiCl_2$ and 15% by weight $CuCl_2$. In addition, the effects of reaction pressure and temperature on the catalytic performance of 5%$NiCl_2$-15%$CuCl_2$/HMOR catalyst were investigated. The results showed that the conversion of methanol was 84.2% and selectivity to acetic acid and methyl acetate was 73.5% and the yield of acetic acid and methyl acetate was 61.9%, under optimal reaction conditions of P = 1.5MPa and T = 623K.

Eastman Chemical In 2000, carbonation of methanol vapor phase with acetic acid and methyl acetate, using gold supported on carbon or activated carbon (1% Au/AC) in the presence of methyl iodide under operating conditions at 240 °C and 17 °C, CO/H_2 load [34]. The activity of the prepared catalyst was close to that of iridium catalysts. XRD analysis showed that the diameter of the gold particles for the two prepared catalysts is 12 and 28 nm. Due to the presence of CH_3I during the carbonylation reaction, small clusters of gold containing 2 and 3 atoms were observed by iodide $(Au_2I)^{\delta+}$ and $(Au_3I_2)^{\delta+}$ are fixed.

3-6. Catalysis with iridium

In addition to the Cativa^{TM} process, which works with Ir and Ru at 5% by weight of water, the reaction rate increases if high concentrations of methyl acetate are produced, a similar cooperation

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between [IrI$_2$(CO)$_2$] and [PtI$_2$(CO)]. The main role of the platinum promoter is to separate the iodide ligand from [IrI$_3$(CH$_3$)(CO)$_2$]. In the case of platinum, I-adsorption continues through an intermediate species of iridium-platinum nucler, producing the neutral complex [IrI$_2$(CH$_3$)(CO)$_3$] and the anionic species [PtI$_3$(CO)]. Which reproduces [PtI$_2$(CO)$_2$] by losing I (Figure 9) [35].
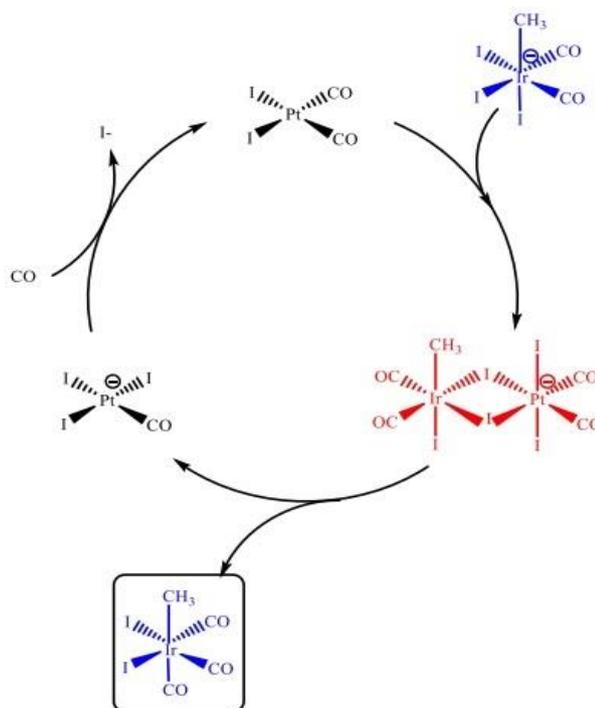

Fig. 9. Detailed pathway of the reaction of platinum on the [IrI$_3$(CH$_3$)(CO)$_2$] intermediate species.

Lauren C. Gregor et al. [36] synthesized iridium complexes containing aza-crown macrophages such as aza-18-crown-6 with the participation of promoters such as Li$^+$, K$^+$, Hf$^+$ in the presence of tetrabutylammonium salt. The carbonylation reaction is accelerated by the removal of ligand I after oxidation of CH$_3$I.

As in the case of Rh catalysts carbon-support, Ir catalysts have also shown interesting performance for vapor phase methanol carbonylation. In an Eastman-registered catalyst based on Ir and a La promoter, the catalyst is a molecular species with distinct sites composed of two metal atoms on an activated carbon base. The Ir-La/AC catalyst showed reactivity and selectivity comparable to similar homogeneous systems. According to mechanical studies, the most probable carbonylation mechanism on Ir-La/AC catalysts is that lanthanum accelerates CO incorporation by absorbing iodine from the active Ir center. Using La as a promoter instead of Ru can help reduce the cost of the catalyst [37]. Recently, Zhou Ren et al. [38] showed that the addition of sulfuric acid groups to the Ir-La/AC catalyst increases methanol carbonylation while maintaining Ir atomic dispersion on the base. They prepared a highly active Ir-La-S/AC catalyst by simultaneously impregnating an activated carbon (AC) carrier with a solution of Ir and La sulfuric acid and compared it with an older Ir-La/AC catalyst. Evaluation of Ir-La-S/AC as a heterogeneous catalyst for methanol to acetyl carbonylation resulted in a maximum TOF (conversion frequency) of 2760 h^{-1}, which is significantly higher than the value obtained by Ir-La/AC catalyst (approximately 1000 h^{-1}). The addition of sulfuric acid during the preparation process results in the formation of more acidic

sites in Ir-La-S/AC than in Ir-La/AC, which play a key role in increasing CO adsorption as a velocity determinant.

4. Conclusions

Methanol carbonylation is one of the oldest homogeneous catalytic reactions that has been developed industrially mainly due to stability issues related to heterogeneous systems. Industrial homogeneous catalysts reported for acetic acid synthesis by liquid phase methanol carbonylation are metal-organic complexes including cobalt, ruthenium, iridium, nickel, and rhodium-based homogeneous catalysts. Although old homogeneous rhodium or iridium catalysts are still used in the industry today, many efforts are being made to improve these catalysts, especially by adding ligands, which can increase their activity. The addition of a ligand can lead to a higher reaction rate, and stability issues often limit this strategy. Recent advances in the design of suitable ligands, mainly based on phosphorus-containing systems, allow the synthesis of highly active and stable rhodium complexes. In this regard, catalytic studies involving multiple recycling or continuous long-term operations should be developed.

In parallel with homogeneous systems, today there are several heterogeneous systems with a particular focus on the development of abundant and inexpensive metal-based catalysts, and the avoidance of promoters. Many studies have shown that the use of mordenites or zeolites as catalysts or catalyst supports leads to relatively high efficiency and selectivity in acetic acid. However, in order for heterogeneous catalysts to work at long reaction rates, they must improve significantly in the future, both in terms of activity, selectivity, and stability.

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