Carbonylation of methanol to produce acetic acid: A versatile reaction to study

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Manuscript received 05 July 2018, accepted 23 July 2018

Carbonylation reaction has aroused much interest in industry for the production of acetic acid. The first methanol to acetic acid carbonylation process was commercialized in 1960 by BASF, which involved iodide-promoted active cobalt catalyst [HCo(CO)₄] and required very high pressures (600 atm) as well as high temperatures (230°C), and the selectivity was 90% only. In order to reduce the severe process parameters, Monsanto commercialized in 1970, a rhodium based homogeneous liquid-phase catalyst [Rh₂(CO)₄] which operated at a pressure of 30–60 bar and at temperatures of 150–200°C with the high selectivity over 99% based on methanol. Subsequently, in 1996, BP Chemicals developed and commercialized the most efficient Cativa process for production of acetic acid, which was based on active iridium catalyst [Ir₂(CO)₄] (with Ru-complex activator) and was able to operate at reduced water content (less than 8 wt.%), compared to that about 14–15 wt.% required by Monsanto process. In order to develop more advantageous catalysts for the carbonylation processes, several efforts are already put forward in the laboratory scale process developments based on metal-complex catalysts of functionalized ligands, such as complexes of the types [Rh(CO)₃Cl(P~O)] and [Rh(CO)Cl(P~O)₂] (P~O = 2-Ph₂PCH₂COOCH₃) which showed efficient catalytic carbonylation reactions with high Turn Over Number (TON). Iridium based catalytic carbonylation of methanol, on the other hand, is gaining much industrial importance compared to rhodium based catalyst because of several advantages. Interesting heterogeneous catalytic process for carbonylation of methanol are also in progress. This brief review focuses on the importance and progress of carbonylation reaction of methanol to produce acetic acid starting from the initial processes to the state-of-the-art technology and also laboratory scale processes based on metal-complex or heterogeneous catalysts including our recent research results and implications.

Keywords: Carbonylation reaction, acetic acid, BASF process, Monsanto process, Cativa process, homogeneous catalysis, heterogeneous catalysis.

Introduction

Carbonylation of methanol to produce acetic acid catalysed by homogeneous metal complexes is the most successful industrial applications¹-⁵. Currently, global annual production of acetic acid is about 15 million tonnes⁶a. Originally, acetic acid (ethanoic acid) was produced by aerobic fermentation of ethanol, which is still the major process for the production of vinegar (8–10 % acetic acid). Direct conversion of methane to acetic acid using rhodium trichloride as the catalyst was reported⁶b wherein the reaction proceeds in an aqueous medium at a temperature of around 100°C, and gives high yields of acetic acid. This reaction may be a potential industrial means to convert methane directly to acetic acid. The major use of acetic acid is an ingredient for production of variety commercial chemicals like vinyl acetate monomer (VAM), acetic anhydride, as a solvent for purified terephthalic acid (PTA) production besides other applications. During the last six decades, three major industrial catalytic carbonylation systems were commercialized starting from the catalysts based on cobalt (BASF process, 1960) to rhodium (Monsanto process, 1970) and lastly iridium (BP Chemical process i.e. Cativa, 1996)⁵. Among the three commercial processes, a very high pressure of about 600 bar of CO is required for the BASF process in order to stabilize the cobalt carbonyl catalyst at high reaction temperatures of about 250°C⁴. At present, the industrial processes for the production of acetic acid are dominated by carbonylation of methanol [eq. (1)]. Therefore, significant cost advantages resulted from the use of carbon monoxide (produced from natural gas) and methanol (prepared from synthesis gas) as feedstocks⁴.

\[
\text{CH}_3\text{OH} + CO \rightarrow CH₃COOH + \Delta H
\]
Carbonylation of methanol can be catalysed by different metals (Ni, Co, Rh and Ir) complexes involving methyl iodide as activator or co-catalyst. In addition to acetic acid, carbonylation of methanol also gives rise to the formation of methyl acetate [eq. (2)].

\[
CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O \tag{2}
\]

One of the main reactants of carbonylation reaction is carbon monoxide (CO) gas which was discovered in 1776 by Lassone. The gas is colourless, odourless, tasteless, flammable, reactive and highly toxic. Other characteristics of CO are: bond length: 112.8 pm, bond energy: 257 kcal/mol, dipole moment: 0.112 D, and insoluble in water (26 mg/L). Carbonylation reactions lead to the incorporation of CO into diverse organic and inorganic molecules to form different important classes of compounds. CO molecule has gained immense interest as C1 unit building block through C-C bond formations in many catalytic carbonylation reactions. CO being strong \( \delta^- \)-donor and \( \pi \)-acceptor acts as a ligand in transition-metal complexes forming metal-CO bond and these interactions lead to activation of the CO, making it susceptible to be attacked by nucleophiles and also to intramolecular ligand migration reactions leading to the key C-C bond formation in many catalytic carbonylation reactions.

The CO gas may be prepared by the following processes:

1. By burning elemental carbon in restricted supply of oxygen gas.
   \[ C + O_2 \rightarrow CO \]
2. Reduction of carbon dioxide with coke.
   \[ CO_2 + \text{Coke} \rightarrow CO \text{ at } 800^\circ C \]
3. Dehydration of formic acid (small scale for laboratory preparation).
   \[ \text{HCOOH} + \text{H}_2\text{SO}_4 \rightarrow \text{CO} + \text{H}_2\text{O} \text{ at } 100^\circ C \]
   \[ \text{Coke or CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \text{ at } 900^\circ C \]

Methanol may be produced from synthesis gas:

\[ \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} \]

In order to develop more advantageous catalysts for the carbonylation processes, several efforts are already put forward in the laboratory scale processes based on metal-complex catalysts of functionalized phosphorus and nitrogen containing ligands, such as complexes of the types \([\text{Rh(CO)}_2\text{Cl(P\text-O)P}^\text{3}_2\text{H}_4\text{COOCH}_3]\) which showed efficient catalytic carbonylation reactions of methanol to acetic acid/ester with high Turn Over Number (TON). Iridium based catalytic carbonylation of methanol, on the other hand, is gaining much industrial importance compared to rhodium based catalyst because of several advantages. This brief review focuses on the importance and progress of carbonylation reaction of methanol to produce acetic acid starting from the initial processes to the state-of-the-art technology and also laboratory scale processes based on metal-complex and solid state heterogeneous catalysts including our recent research results and implications.

**Carbonylation of methanol**

**Industrial processes:**

**The cobalt-based BASF process:**

The first industrial process for carbonylation of methanol to produce acetic acid was commercialized in 1960 by BASF. The process was based on iodide-promoted cobalt catalyst and required very high pressures of about 600 atm as well as high temperatures of 230°C, and gave about 90% selectivity.

The active catalytic specie was \([\text{HCo(CO)}_4]\) which could be prepared from the reactions eq. (3) and eq. (4).

\[
\begin{align*}
2\text{CoI}_2 + 2\text{H}_2\text{O} + 10\text{CO} & \rightarrow \text{Co}_2\text{(CO)}_9 + 4\text{HI} + 2\text{CO}_2 \tag{3} \\
\text{Co}_2\text{(CO)}_9 + \text{H}_2\text{O} + \text{CO} & \rightarrow 2[\text{HCo(CO)}_4] + \text{CO}_2 \tag{4}
\end{align*}
\]

The Co-based catalytic carbonylation is presented in Fig. 1. The presence of iodide is necessary in order to convert methanol into methyl iodide prior to carbonylation. Therefore, the actual substrate of carbonylation is methyl iodide. The reaction rate depends on the carbon monoxide pressure which is responsible for high conversion. Cobalt catalysts can also be used for the carbonylation of higher alcohols, such as benzyl alcohol.
The rhodium-based Monsanto process:

The Monsanto process for production of acetic acid by carbonylation reaction is based on a rhodium catalyst and operates at a pressure of 30–60 bar and at temperatures of 150–200°C and gives selectivity of over 99% based on methanol. The catalytic cycle of this homogeneous catalytic carbonylation reaction consisting of six steps is shown in Fig. 2. The major reactions involved are (i) oxidative addition, (ii) migratory insertion, (iii) ligand (CO) insertion, and (iv) reductive elimination. The catalytic cycle of methanol carbonylation was proposed on the basis of analysis of reactants and intermediates. The active catalytic species cis-[Rh(CO)\(_2\)I\(_2\)]\(^–\) interacts with the substrate CH\(_3\)I resulting in the formation of the hexacoordinated complex [(CH\(_3\)I)Rh(CO)\(_2\)I\(_3\)]\(^–\) which is unstable and leading to the formation of isomeric pentacoordinated acetyl complex [(CH\(_3\)CO)Rh(CO)I\(_3\)]\(^–\) as a result of the migration of the methyl group to the CO ligand. The rhodium acetyl complex was isolated and characterized by X-ray crystallography. The rhodium acetyl anion was found to form dimers through a very weak Rh-I-Rh bridge (with a rhodium-iodine distance of 3.0 Å, as compared to 2.7 Å commonly found for Rh-I bonds). The rhodium acetyl complex reacts rapidly with CO to form the six-coordinated dicarbonyl complex with terminal CO and subsequently elimination of CH\(_3\)COI occurs with the generation of [Rh(CO)\(_2\)I\(_2\)]\(^–\) for continuing the next catalytic cycle. Acetic acid is finally formed by hydrolysis of acetyl iodide and generating HI to react with methanol to produce methyl iodide which undergoes oxidative addition with the active catalyst. Therefore, it is interesting to note that although the overall reaction is designated as carbonylation of methanol but the substrates CH\(_3\)OH and CO do not undergo direct interaction to produce acetic acid. The kinetics of the overall carbonylation process are zero order in CH\(_3\)OH and CO but first order in rhodium catalyst and methyl iodide promoter.

The rate of methanol carbonylation depends on the concentrations of both the rhodium complex and methyl iodide. The reaction rate is independent of the methanol concentration and the carbon monoxide pressure. The rate determining step is probably the oxidative addition of methyl iodide to the metal center of the rhodium complex [Rh(CO)\(_2\)I\(_2\)]\(^–\), because the reaction rate is essentially of first order in both catalyst and methyl iodide concentrations under normal reaction conditions. The requirement of water is about 14–15 wt.% in order to achieve high catalyst activity and also to maintain good catalyst stability.

The [Rh(CO)\(_2\)I\(_2\)]\(^–\) ion can also catalyze the water gas-shift reaction (WGSR). The catalytic cycle for the WGSR is shown in Fig. 3. Oxidation of Rh\(^{I}\) to Rh\(^{III}\) takes place by the reaction of [Rh(CO)\(_2\)I\(_2\)]\(^–\) with HI to give initially the hydride, [Rh(CO)\(_2\)I\(_3\)]H\(^–\) which further reacts readily with HI to release H\(_2\) and also to form [Rh(CO)\(_2\)I\(_4\)]\(^–\). In order to maintain the rhodium catalyst in its active form, relatively high water concentrations are maintained in the process, which accelerate the reduction of the intermediate 3 leading back to the active Rh\(^{I}\) catalyst (1) and thus completing the WGSR cycle (Fig. 3).
The reaction cycle can be broken down into two basic reactions [eq. (5) and eq. (6)]:

\[
[Rh(CO)_2I_2]^− + 2HI \rightarrow [Rh(CO)I_4]^− + H_2 + CO \quad (5)
\]

\[
[Rh(CO)I_4]^− + 2CO + H_2O \rightarrow [Rh(CO)_2I_2]^− + CO_2 + 2HI \quad (6)
\]

Thus, the overall reaction is \(CO + H_2O \rightarrow CO_2 + H_2\). It appears that the water gas shift reaction could be a good competitor as a potential side reaction for carbonylation of methanol. The side reaction leading to \(CO_2\) and \(H_2\) is significantly affected by water and hydrogen iodide concentration in the reaction system\(^{16}\). The rhodium catalyst \([Rh(CO)_2I_2]^−\) can also generate acetaldehyde, which may undergo reduction by hydrogen to produce ethanol and subsequently yields propionic acid.

**The iridium-based Cativa process of BP chemicals:**

The Monsanto group found the effectiveness of iodide-promoted iridium catalysts\(^{17}\), and later on substantiated the findings by other researchers\(^{16,18}\). Improved iridium catalyst, in combination with a promoter metal such as ruthenium, has higher activity and selectivity than reported in previous iridium systems\(^{19}\). The production of acetic acid using the iridium catalyst system i.e. Cativa process has been commercialized in 1996 by BP Chemicals. Much more amount of iridium is required to maintain an activity comparable to the rhodium catalyst-based processes, the catalyst process is able to operate at reduced water levels of about 8 wt.% compared to about 14–15 wt.% for the the Monsanto process.

The major advantage of the iridium-based process is the high stability of the iridium catalyst species. The iridium catalyst was also found to remain stable under a wide range of conditions. Iridium is much more soluble than rhodium in the reaction system, and therefore leading to much higher reaction rates.

The main difference between the rhodium- and iridium-based catalytic cycles has been determined by Maitlis et al.\(^8\) wherein, the rhodium based cycle involves only anionic intermediates, the iridium-based cycle, on the other hand, involves both anionic and neutral intermediates. The iridium-based cycle (Fig. 4) is similar to the rhodium-based cycle, but operates with different kinetics, responsible for the advantages of the Cativa process over the Monsanto process. The oxidative addition of methyl iodide to the iridium center is about 150 times faster than the analogous reaction with rhodium\(^8\). This represents a dramatic improvement in reaction rates, as this step is now no longer rate determining (as in the case of rhodium). The slowest step in the iridium-based cycle is the substitution of an iodo ligand by carbon monoxide (2nd step in Fig. 4). It suggests that the inclusion of species capable of assisting in removing iodide should promote the rate-limiting step. In fact, promoters can be used to enhance the performance of the iridium catalyst. The presence of a promoter leads to a substantial increase in the propor-

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**Fig. 3.** Catalytic cycle for WGSH reaction catalysed by \([Rh(CO)_2I_2]^−\).

**Fig. 4.** Catalytic cycle for carbonylation of methanol catalysed by Ir-complex in presence of activator in Cativa process.
HPIR spectroscopy shows that in situ nickel-complex catalyst: Homogeneous catalysts: Laboratory processes

**Nickel-complex catalyst:**

A variety of nickel carbonyl complexes are catalytically active for the carbonylation of methanol in the presence of iodine. The active complex Ni(CO)$_4$ may be prepared as shown in eq. (7).

$$\text{NiI}_2 + \text{H}_2\text{O} + 5\text{CO} \rightarrow \text{Ni(CO)}_4 + 2\text{HI} + \text{CO}_2$$

(7)

The catalytic activities of Ni(CO)$_4$ in presence of CH$_3$I and CO gas pressure are presented in the catalytic cycle (Fig. 5). The first step is the oxidative addition of CH$_3$I to Ni centre and subsequently CO addition and insertion occurs to form acyl complex which in turn eliminates CH$_3$COI. The resulting CH$_2$COI is hydrolysed to form acetic acid and HI which reacts with methanol to form CH$_3$I and H$_2$O to complete the cycle.

Usually nickel catalysts require rather high pressure and temperature conditions. Although nickel catalysts have the advantage of being much cheaper and easy to stabilise at low water concentrations, no commercialisation has been possible so far, because Ni(CO)$_4$ is a very toxic and volatile compound. Other Ni-complexes of phosphines were also tried as catalysts but without much success.

**Ligand based metal-complex catalysts:**

The major industrial production of acetic acid is done by the catalytic carbonylation of methanol catalysed Rh (Monsanto process) or Ir (Cativa) based catalysts. Considerable efforts are being made in order to improve the catalyst by incorporating different ligands into the coordination sphere of the metal catalyst. Among these, ligands containing functionalized P and N are more widely studied because of their $\sigma$-bonding and $\pi$-back bonding capacity (for P atom).
through which they can stabilize low valent metals or strong σ-bonding (for N atom) to enhance electron density on the metal centre. As a result, the metal center becomes more susceptible to oxidative addition, which is the primary step of carbonylation reaction.\textsuperscript{8,22–32}

**Phosphine-based ligands promoters:**

The catalytic rate can be improved much by introducing strongly donating ligands that increase the nucleophility of the Rh center, because the rate-determining step for rhodium/iodide-catalyzed methanol carbonylation is the oxidative addition of CH\(_3\)I to Rh(CO)\(_2\)I\(_2\). Thus, by increasing the electron density on the metal centre should increase the rate of oxidative addition and hence the overall rate of production of acetic acid. There have been several attempts to modify [Rh(CO)\(_2\)I\(_2\)]\(^{-}\) by incorporating electron donating ligands, for instance, Baker \textit{et al.}\textsuperscript{33} used [RhI(CO)-(P\(_3\)PCH\(_2\)P(S)Ph\(_2\)]) to enhance the rate of carbonylation at 185°C. Cavell and co-workers\textsuperscript{34} prepared complexes of the form, [RhCl(CO)(PPh\(_2\)CH\(_2\)PPh\(_2\)NR)], where R is a substituted phenyl group. Similarly, Dilworth \textit{et al.}\textsuperscript{35} used rhodium(i) carbonyl complexes containing phosphinothioate and thioether ligands to promote the rate of carbonylation of methanol under the conditions of 70 bar and 185°C. Cole-Hamilton and co-workers\textsuperscript{36,37} reported some interesting Rh-complexes such as [RhI(CO)(PEt\(_3\)\(_2\)] which is more active for the carbonylation of methanol to acetic acid than [Rh(CO)\(_2\)I\(_2\)]. At 25°C, the rate of oxidative addition of CH\(_3\)I for [RhI(CO)(PEt\(_3\)]) is 57 times faster than that for [Rh(CO)\(_2\)I\(_2\)]. Despite the high initial activity of the Rh/PEt\(_3\) system, catalyst degradation occurred due to loss of the phosphine ligands. A number of other types of ligands including modified pyridines, phenols, and benzoic acids have been tested by the group of Dutta in rhodium-catalyzed methanol carbonylation\textsuperscript{38–46}.

Heterodifunctional phosphane derivatives have received considerable attention. In metal complexes containing ligands such as, P-O, where the tertiary phosphorous atoms are strongly bonded with the metal centre and the oxygen donors tend to form a weak chelate metal-oxygen bond which may be cleaved reversibly and thus tends show an ‘Opening and closing mechanism’. Thus, the P-O ligands are known as \textit{hemilabile} ligands. Lindner and co-workers investigated\textsuperscript{47}, the \textit{hemilabile} ether-phosphines such as Ph\(_2\)PCH\(_2\)CH\(_2\)OME in carbonylation of methyl iodide catalyzed by cationic ether-phosphine rhodium complex. An additional advantage of such P-O ligands is their ability to increase the electron density at the metal centre by metal-oxygen interaction facilitating the oxidative addition and reductive elimination of the in catalytic reactions. In a more recent contribution on this theme, Dutta and co-workers\textsuperscript{48} reported a through investigation on a functionalized triarylphosphane ligand, PPPh\(_2\)(C\(_6\)H\(_4\)2- CO\(_2\)Me), that contains an \textit{ortho}-ester substituent. The complexes [Rh(CO)Cl(2-Ph\(_3\)PC\(_6\)H\(_4\)COOMe)]\(_2\) (1), and trans-[Rh(CO)Cl(2-Ph\(_3\)PC\(_6\)H\(_4\)COOMe)]\(_2\) (2), were synthesized by the reaction of the dimer [Rh(CO)\(_2\)Cl\(_2\)] with 2 and 4 molar equivalents of 2-(diphenylphosphino)-methyl benzoate. The complexes 1 and 2 show terminal v(CO) bands at 1979 and 1949 cm\(^{-1}\) respectively indicating high electron density at the metal centre. The molecular structure of the complex 2 indicates that rhodium atom is in a square planar coordination environment with the two phosphorus atoms trans to each other; the ester carbonyl oxygen atom of the two phosphine ligands points towards the rhodium centre above and below the vacant axial sites of the planar complex. The rhodium-oxygen distances (Rh-O(49) 3.18 Å; Rh-O(19) 3.08 Å) and the angle O(19)-Rh-O(49) 179° indicate long range intramolecular secondary Rh-O interactions leading to a pseudo-hexacoordinated complex. The complexes 1 and 2 undergo oxidative addition (OA) reactions with CH\(_3\)I to produce acyl complexes [RhI(CO)(2-Ph\(_3\)PC\(_6\)H\(_4\)COOMe)] (3) and trans-[Rh(CH\(_3\)I)Cl(2-Ph\(_3\)PC\(_6\)H\(_4\)COOMe)] (4), and the kinetics of the reactions reveal that the complex 1 undergoes faster OA reaction than that of the complex 2 (Fig. 6). The catalytic activity of the complexes 1 and 2 in the carbonylation of methanol were higher than that of the well known species [Rh(CO)\(_2\)I\(_2\)]\(^{-}\} and the complex 1 shows higher activity than 2 (Table 1) under the reaction conditions: Temp. 130 ± 5°C and pressure 35±2 bar.\textsuperscript{48}

Wegman and co-workers\textsuperscript{49} found that a bidentate phosphane oxide, dppeO gave a rhodium catalyst that had good activity for methanol carbonylation under mild conditions (turnover frequency (TOF) 400 h\(^{-1}\), 80°C, 3 bar CO). Mechanistic studies indicated that the dppeO ligand is hemilabile, and [Rh(CO)\(_2\)(dppeO)]Cl was the only Rh species observed under catalytic conditions by \textit{in situ} HPIR spectroscopy.
Rhodium-nitrogen and nitrogen-oxygen based ligands complexes as promoters:

Rhodium(I) and iridium(I) carbonyl complexes of nitrogen (N) and nitrogen-oxygen (N-O) donor ligands are of much interest in recent time because of their structural novelty, reactivities and catalytic applications. Different types of N and N-O donor ligands like pyridine, hydroxypyridines, pyridine alcohols, pyridine aldehydes, pyridine carboxylic acids, pyridine esters, benzoylpyridines, aminophenols, aminobenzoic acids etc. form a wide variety of interesting metal complexes of rhodium and iridium. The catalytic carbonylation of methanol exhibited by different rhodium carbonyl complexes are efficient and show high TON. Iridium based catalytic carbonylation of methanol is gaining much industrial impor-

Fig. 6. Oxidative reaction and migration insertion of the complexes 1 and 2 (Adapted from Ref. 48).
tance compared to rhodium based catalyst because of several advantages. In contrast to the P-atom, N-atom has only σ-donor (and no or very weak π-acceptor)\(^{50}\) properties due to which M-N bond has more prominent ionic character compared to the M-P bond\(^ {46,51} \). The σ-donor character of nitrogen makes the metal more susceptible to oxidative addition which is a part of the cabonylation catalytic cycle. Chelating ligands containing N-O donors are also reported for example picolinic acid is known to bind with metal ions as a bidentate N-O donors forming a stable five member chelate ring\(^ {52-55} \). Interestingly, both the donor sites bear significantly different bonding nature. The N-atom which is a part of benzene ring and the O-atom of the side chain of the benzene ring are ‘Hard’ donors having different hardness stabilize metal centers in their high oxidation states. The combination of atoms of unequal hardness in the same ligand framework may offer the advantage of providing free coordination sites by being detaching the weaker metal-ligand bond reversibly (hemi-labile) from the coordinating site and make space for the incoming substrate. Due to strong σ-donor capability such N-donor ligands enhance the nucleophilicity of the metal center which in turn increases the catalytic activity of the complexes. Catalysts that do not have phosphate ligands can offer some advantages as oxidation of phosphines can lead to catalyst deactivation, catalyst durability may be improved in phosphate-free catalysts\(^ {56} \).

In our work\(^ {41} \), it was reported that the complexes, [Rh(CO)\(_2\)ClL] (1a-1g), where L = 2-methylpyridine (a), 3-methylpyridine (b), 4-methylpyridine (c), 2-phenylpyridine (d), 3-phenylpyridine (e), 4-phenylpyridine (f), pyridine (g) undergo oxidative addition (OA) with various electrophiles like CH\(_3\)I, to give to complex of the type [Rh(CO)(COCH\(_2\))ClL]. In the carbynylation reaction of methanol to form acetic acid and its ester catalyzed by the rhodium complexes cis-[Rh(CO)\(_2\)Cl(L)] (L = a-g) in presence of CH\(_3\)I under the reaction conditions: 4 ml of methanol, 1 ml of CH\(_3\)I, 1 ml of H\(_2\)O, [Rh] = 0.054 mmol, CO 20 bar at 130\(^\circ\)C for 1 h and the TON per hour for methanol conversion to carbonylated products follows the order 1b > 1c > 1g > 1a > 1f > 1e > [Rh(CO)\(_2\)Cl]\(^+\) > 1d (Table 2). A carbynylation catalytic cycle for the pyridine based rhodium system is proposed (Fig. 7) which is closely resembles the well established cycle for the Monsanto catalyst [Rh(CO)\(_2\)Cl]\(^+\). The formation of methyl acetate from the reaction of acetic acid and methanol is not shown in the catalytic cycle. The overall rate of carbynylation is dependent on the rate-determining OA step of methyl iodide to Rh\(^+\) center. It appears from the Table 2, that the Rh-complexes containing N-donor ligands exhibit, in general (except the case of 1d), higher efficacy in carbynylation reaction of methanol compared to the Monsanto’s species.

### Table 1. Results of carbynylation reaction of methanol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Total conversion (%)</th>
<th>Methyl acetate (%)</th>
<th>Acetic acid (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)(_2)Cl] (^+)</td>
<td>1.5</td>
<td>64</td>
<td>52.0</td>
<td>12.0</td>
<td>1052</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>95</td>
<td>28.7</td>
<td>65.3</td>
<td>1563</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>82</td>
<td>30.9</td>
<td>51.1</td>
<td>1349</td>
</tr>
</tbody>
</table>

\(^{a}\)Conversion = \([\{CO consumed (mol)\}/[CO charged (mol)]]\)×100. CO consumption was determined from analysis of products by GC. \(^{b}\)Yields of methyl acetate and acetic acid were obtained from GC analyses. \(^{c}\)TON = [amount of product (mol)]/[amount of catalyst (Rh mol)]. \(^{d}\)Formed from added [Rh(CO)\(_2\)Cl\(_2\)] under the catalytic condition.

### Table 2. Yields of carbynylation reaction of methanol

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Acetic acid (%)</th>
<th>Methyl acetate (%)</th>
<th>Total conversion (%)</th>
<th>TON (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)(_2)Cl] (^+)</td>
<td>4.07</td>
<td>37.45</td>
<td>41.52</td>
<td>760</td>
</tr>
<tr>
<td>1a</td>
<td>7.22</td>
<td>41.08</td>
<td>48.30</td>
<td>884</td>
</tr>
<tr>
<td>1b</td>
<td>12.35</td>
<td>53.55</td>
<td>65.90</td>
<td>1206</td>
</tr>
<tr>
<td>1c</td>
<td>10.72</td>
<td>48.68</td>
<td>59.40</td>
<td>1087</td>
</tr>
<tr>
<td>1d</td>
<td>3.42</td>
<td>36.73</td>
<td>40.15</td>
<td>735</td>
</tr>
<tr>
<td>1e</td>
<td>6.16</td>
<td>37.20</td>
<td>43.36</td>
<td>793</td>
</tr>
<tr>
<td>1f</td>
<td>5.54</td>
<td>40.33</td>
<td>45.87</td>
<td>840</td>
</tr>
<tr>
<td>1g</td>
<td>5.90</td>
<td>43.88</td>
<td>49.78</td>
<td>911</td>
</tr>
</tbody>
</table>

\(^{a}\)TON = mole of product per mole of catalyst. \(^{b}\)Formed from added [Rh(CO)\(_2\)Cl\(_2\)] under catalytic condition.

Sarmah et al. reported\(^ {45} \) carbynylation of methanol to acetic acid and its ester in presence of CH\(_3\)I under CO catalyzed by dicarbonylrhodium(l) complexes [Rh(CO)\(_2\)ClL] (1a-1b), where L = pyridine-alcohol ligands of the type 2-hydroxymethylpyridine (a), 3-hydroxymethylpyridine (b) and 4-
Dutta: Carboxylation of methanol to produce acetic acid: A versatile reaction to study

The complexes $1$ undergo OA with various alkyl halides (RI) like CH$_3$I, C$_2$H$_5$I to produce Rh$^{	ext{III}}$ complexes of the type [Rh(CO)(COR)IClL], where R = -CH$_3$, -C$_2$H$_5$. The rate of OA of CH$_3$I with these three complexes shows the order $1b > 1c > 1a$. The catalytic activity of these complexes in carboxylation of methanol, in general, is higher (TON = 649–542) than that of the well-known species [Rh(CO)$_2$I$_2$]$^-$ (TON = 526) measured at the same reaction conditions and follows the order $1c > 1a > 1b$.

Borah et al. reported the new complexes of the type [Rh(CO)$_2$ClL] ($1a$-$1c$), where L = 2-benzoylpyridine (a), 3-benzoylpyridine (b) and 4-benzoylpyridine (c) have been synthesized and characterized. Oxidative addition (OA) of $1a$-$1c$ with CH$_3$I, afford penta-coordinated Rh$^{	ext{III}}$ complexes, [Rh(CO)(COCH$_3$)ClIL]. Kinetic data for the reaction of $1a$-$1c$ with CH$_3$I indicate a pseudo-first order reaction. The complexes exhibit high catalytic activity in the carboxylation of methanol to acetic acid and its ester and show a higher TON = 1529–1748 than the well known commercial species [Rh(CO)$_2$I$_2$]$^-$ (TON = 1000) (Table 3).

Sharma et al. reported the carboxylation activity of methanol to acetic acids catalysed by the complexes [Rh(CO)$_2$ClL], where L = 2-aminophenol (a), 3-aminophenol (b) and 4-aminophenol (c). The ligands are coordinated to the metal center through an N-donor site. The catalytic activity of the complexes in carboxylation of methanol, in general, is higher (TON = 1189–1456) than the species [Rh(CO)$_2$I$_2$]$^-$ (TON=1159). Sharma et al. also reported the catalytic activity of dicarbonyl-rhodium complexes of aminobenzoic acid ligands on carboxylation of methanol and ethanol. Rhodium(I) complexes of the type, [Rh(CO)$_2$ClL], where L = 2-aminobenzoic acid (a), 3-aminobenzoic acid (b) and 4-aminobenzoic acid (c), have been synthesised. The complexes show higher catalytic activity for carboxylation of methanol than that of the well known species [Rh(CO)$_2$I$_2$]$^-$.

Das et al. reported some interesting rhodium(I) carbonyl complexes of the type [Rh(CO)$_2$ClL], where L = αN-diphenyl nitrotrone (a), α-styryl-N-phenyl nitrotrone (b), N,N'-diphenyldinitrione (c) and α-(2-

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**Table 3. Results of carboxylation reactions of methanol catalysed by [Rh(CO)$_2$ClL]**

<table>
<thead>
<tr>
<th>Catalysts precursors</th>
<th>Time (h)</th>
<th>Acetic acid (%)</th>
<th>Methyl acetate (%)</th>
<th>Total conversion (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)$_2$I$_2$]$^-$</td>
<td>1</td>
<td>10.3</td>
<td>41.8</td>
<td>52.1</td>
<td>1000</td>
</tr>
<tr>
<td>1a</td>
<td>1</td>
<td>32.3</td>
<td>47.2</td>
<td>79.5</td>
<td>1529</td>
</tr>
<tr>
<td>1b</td>
<td>1</td>
<td>58.8</td>
<td>32.1</td>
<td>90.9</td>
<td>1748</td>
</tr>
<tr>
<td>1c</td>
<td>1</td>
<td>46.3</td>
<td>34.2</td>
<td>80.5</td>
<td>1548</td>
</tr>
</tbody>
</table>

*Yield of methyl acetate and acetic acid were obtained from GC analysis.
furyl)-N-phenylnitrone (d) act as efficient catalyst precursors showing TON in the range 1200–1400 per 90 min for carbonylation of methanol to produce acetic acid and its ester at temperature 150±10°C and pressure 20 bar. Deb and Dutta, reported the complexes [Rh(CO)Cl(L)] (1a,1b) and [Rh(CO)2Cl(L)] (1c,1d), where L stands for 9,9-dimethyl-4,5-bis-(diphenyl-phosphino)xanthenes-[Xantphos] (a), bis(2-diphenylphosphino-phenyl)-ether [DPEphos] (b) and their corresponding dioxide analogues Xantphos dioxide (c), DPEphos dioxide (d). The catalytic activity of 1a-1d for the carbonylation of methanol to acetic acid and its ester was evaluated at different CO pressure 15, 20 and 33 bar at 130°C and a Turn Over Frequency (TOF) upto 1768 was obtained compared to that of the well-known commercial species [Rh(CO)2I2] (TON = 1000) under the similar experimental conditions. Typical examples are shown in Fig. 8.

Iridium carbonyl complexes of nitrogen and nitrogen-oxygen donor ligands as promoters:

The use of Vaska’s complex trans-[Ir(PPh3)2(CO)Cl] and others in the hydrogenation of alkenes as well as the polymerization of styrene and carbonylation of methanol to acetic acid are illustrative examples of the applications of Ir1 complexes in catalytic processes19a,58–60. Dutta and co-workers reported the reaction of dimeric precursor [Ir(CO)2Cl]2 with two molar equivalent of the pyridine ester ligands (L) like methyl picolinate (a), methyl nicotinate (b), methyl isonicotinate (c), ethyl picolinate (d), ethyl nicotinate (e) and ethyl isonicotinate (f) affords the tetra coordinate neutral complexes of the type [Ir(CO)2ClL]. The OA of the complexes with different electrophiles such as CH3I, C2H5I and I2 undergo decarbonylation of one CO group to generate the oxidized products of the type [Ir(CO)RCIL], where R = -CH3; -C2H5 and [Ir(CO)Cl2L]. Such complexes are likely to be efficient catalysts in carbonylation of methanol using suitable activators. Pardey et al. reported WGSR activity for the iridium complexes, cis-[Ir(CO)2L2](PF6) (L = pyridine based ligands). Turnover frequency (H2) values follow the order 4-picoline > 3-picoline > pyridine > 3,5-lutidine > 2-picoline > 2,6-lutidine under 1.9 atm of CO at 100°C; [Ir] = 10 mM. However, no catalytic carbonylation reaction was reported.

Heterogeneous catalysts:

Carbonylation of methanol by using Rh- and Ir-based catalysts stands out as the more relevant industrial processes for the worldwide production of acetic acid and methyl acetate and is successfully applied by many chemical companies in homogeneous systems, i.e. the Monsanto and Cativa processes, as well as in heterogeneous systems, i.e. the Acetica and BP SaaBre processes4,19a,62–65. The homogeneous systems present a major drawback, because of the complexity and cost of the manufacturing process such as

Fig. 8. Influence of phosphorus and oxygen donor diphosphine ligands in carbonylation of methanol.
the recycling of catalyst from corrosive product mixture\textsuperscript{4}. On the other hand, in the heterogeneous systems, the catalysts are easily separated from the reaction mixture and can be used in continuous liquid- and gas-phase reactions. However, the development of heterogeneous catalysts with high efficiency and long-term stability is considerably challenging tasks because of several factors.

Direct carbonylation of methanol into methyl acetate and acetic acid using Rh-based heterogeneous catalysis is of great interest due to the effective levels of activity and stability.

The heterogenization of a Rh-based molecular catalyst on a charged 1,3-bis(pyridyl) imidazolium-based covalent triazine framework (Rh-bpim-CTF) was carried out\textsuperscript{62} to have a single-site distribution of metal molecular species throughout the support by its ligation to abundant N atom sites for carbonylation of methanol. The Rh-bpim-CTF catalyst exhibited an excellent catalytic conversion of methanol up to 93\%, corresponding to the TOF of 2100 h\textsuperscript{–1} and productivity of 124.4 mol kg\textsuperscript{–1} h\textsuperscript{–1} with selectivities of 56\% for acetic acid and 44\% for methyl acetate at 240ºC temperature and under 10-bar pressure.

The development of efficient heterogeneous catalytic systems through the heterogenization of metal complexes on various catalytic supports has achieved remarkable progress\textsuperscript{66–77}. The well-defined ligand sites on the supports in Rh catalyzed methanol carbonylation could provide abundant binding sites for the metal complexes and enhanced the nucelophilicity of the Rh\textsuperscript{I} active site, thereby increasing the catalytic activity in such reactions. The positively charged ligand structures on the surface of the support could drastically increase the stability of the catalyst even at high temperatures and pressures through the electrostatic interaction with the catalytic active species, i.e. $[\text{Rh}(\text{I})\text{CO}_2\text{Cl}_2]^-$. In general, compared to the Monsanto’s homogeneous catalytic system, the Rh-heterogeneous methanol carbonylation displays lower activity and stability. Recently, Ren\textit{et al}. reported\textsuperscript{66} that a single site catalyst Rh-POL-PPh\textsubscript{3} (POL = porous organic polymers) could be successfully prepared by impregnation of the Rh\textsubscript{2}(CO)\textsubscript{4}Cl\textsubscript{2} and applied to heterogeneous methanol carbonylation in a continuous fixed-bed reactor for the first time. Due to single site Rh species and the electron-donating effect of P ligands and the strong multi-coordination bonds between Rh and P, the Rh-POL-PPh\textsubscript{3} catalyst exhibited a little higher TOF of 1550 h\textsuperscript{–1} than that of optimized Monsanto process and maintained relatively stable activity for near 180 h under 2.5 MPa, and at 195ºC. Therefore, POL-PPh\textsubscript{3} plays an important role to make stable support and also in promoting methanol carbonylation process.

Bifunctional catalysts comprising Rh(CO)(Xantphos) exchanged phosphotungstic acids of general formulas [Rh(CO)(Xantphos)]\textsuperscript{+},[H\textsubscript{3}n PW\textsubscript{12}O\textsubscript{40}]\textsuperscript{3–} have been synthesized\textsuperscript{60} over silica supports which exhibit tunable activity and selectivity toward direct vapor phase methanol carbonylation under mild reaction conditions: 1 bar and 200ºC. The optimal Rh:acid ratio = 0.5, with higher rhodium concentrations increases the selectivity to methyl acetate over dimethyl ether.

There is a scope to develop more sustainable and ‘Green’ processes to overcome the inherent drawbacks. Well-designed cross-linked copolymers were prepared and used\textsuperscript{65} as support for the simultaneous immobilization of rhodium and iodide species. The resulting catalyst was highly active in CH\textsubscript{3}I-free methanol carbonylation and methyl acetate was the main product. Methanol was converted (90\%) at 120ºC under a CO pressure of 3.0 MPa for reaction time 180 min. The immobilized active catalytic species exhibits high efficiency in methanol carbonylation and good recyclability. After regenerating the catalyst twice over a fifteen batches test, the catalyst was reusable. The process presents catalyst which is a promising one in sustainable methanol carbonylation. Development of a halide-free heterogeneous catalytic process for methanol carbonylation is of great importance. A ‘Green’ route has been developed for direct synthesis of acetic acid through vapour-phase carbonylation of methanol with a stable, selective, halide-free, and noble metal-free catalyst based on pyridine-modified H-mordenite zeolite\textsuperscript{76}. Methanol conversion and acetic acid selectivity were observed up to 100\% and 95\%, respectively.

Dutta\textit{et al}. recently reported\textsuperscript{77} a functionalized montmorillonite supported rhodium complex which exhibited efficient catalytic carbonylation of methanol. The catalyst precursors, [Rh(CO)\textsubscript{2}Cl-ligand(L)-APTMS-montmorillonite] (1a and 1b, where, a and b correspond to ligand (L)-APTMS-montmorillonite for ligands L = quinoline-2-carboxylic acid (L1) and quinoline-8-carboxylic acid (L2) respectively; APTMS = (3-aminopropyl)-trimethoxysilane), have been synthesised (Fig. 9). The montmorillonite was activated (AT-Mt) by treating with
formic acid under controlled condition to increase the surface area and pore volume prior to functionalization by APTMS and subsequent anchoring with the ligands. The efficacy of the catalysts was evaluated in carbonylation of methanol to acetic acid and found to exhibit catalytic conversion up to 99.9% when the reaction was carried out for 3 h at 130±2ºC with corresponding CO pressure 33±2 bar. After the reaction, the catalyst was recovered by simple filtration and the products were analyzed by GC. The catalysts were recovered and reused for several runs without any significant loss of catalytic efficiency.

A novel heterogeneous rhodium-incorporated graphitic carbon nitride (g-C$_3$N$_4$ matrix) has been developed for a liquid-phase carbonylation of methanol to acetic acid to overcome the disadvantages of the commercialized Rh-based homogeneous catalysts. The heterogeneous catalyst showed a superior catalytic activity in a liquid-phase carbonylation with acetic acid yield above 82% under the reaction conditions of 140ºC and CO pressure of 4.0 MPa. A higher dispersion of the incorporated rhodium nanoparticles in the g-C$_3$N$_4$ matrix with a small crystallite size was responsible for the higher catalytic activity.

Heterogeneous analogs to homogeneous catalysts is of great importance to many industrial processes. Acetic acid synthesis through the carbonylation of methanol is one such process where it is difficult to separate homogeneous Ir-based catalyst. A promising single-site Ir-La/C heterogeneous catalyst has been developed for methanol carbonylation. The La promoter in the Ir-La/C catalyst was found to behave similarly to homogeneous promoters by abstracting an iodine from the Ir center and accelerating the CO insertion step. The work provides some key insight into the Ir-La/C single-site catalyst and paves the ways for further design and optimization of single-site heterogeneous catalysts.

Conclusions

Carbonylation of methanol or other organic molecules remains potentially important in academia and industries. The developments and progress of catalytic carbonylation of methanol to produce acetic acid from the laboratory scale to the industrial level are tremendous right from cobalt to rhodium and iridium-based homogeneous catalysts. The efforts continue for more active, selective, and efficient catalysts, having metal center tunable by ligands, or the metal complex catalyst immobilized on a support or metal supported solid state heterogeneous catalysts to simplify product separation techniques. In view of the above, it has become obvious that carbonylation of methanol is a versatile reaction to study and there exists a large scope to develop highly efficient commercial catalyst in respect of stability, conversion, selectivity, reaction kinetics, low pressure, low temperature, reusability etc. to produce acetic acid.

Acknowledgement

The author is grateful to Dr. D. Ramaiah, Director, CSIR-North East Institute of Science and Technology, Jorhat,
Dutta: Carbylation of methanol to produce acetic acid: A versatile reaction to study

Assam, India, for his kind support. The author is also grateful to CSIR, New Delhi, for sanctioning the Emeritus Scientist Scheme (No. 21(1029)/16/EMR-II).

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