

Acetic Acid from the Carbonylation of Chloride Methane Over Rhodium Based Catalysts

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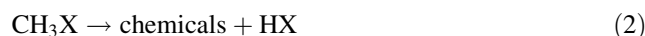
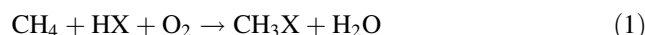
Abstract A new route for the indirect conversion of methane that makes use of the latest advance in methyl chloride production is reported. Acetic acid was produced from the carbonylation of methyl chloride by carbon monoxide over a variety of catalysts. The presence of promoters was crucial for the carbonylation reaction. The yield of acetic acid reached 84.7% with RhCl_3 as catalyst and PPh_3/KI as promoters. The effects of reaction temperature, carbon monoxide pressure, and reaction time were investigated. The possible reaction mechanism was discussed.

Keywords Methane activation · Chloride methane · Carbonylation · Rhodium catalysts

1 Introduction

The conversion of natural gas has attracted much attention as a potential route to obtain chemicals. Methane, the main component of natural gas, however, is intrinsically passive because of its highly symmetrical tetrahedral geometry and strong C–H bonds (439 kJ/mol) [1]. Direct routes for methane conversion, e.g., methane selective oxidation [2, 3], oxidative coupling of methane [4] and methane dehydroaromatization [5], have potential advantages but because of low methane conversion or poor product

selectivity, these processes are not commercialized yet. Current industrial technologies for the production of chemicals from methane are mainly based on an indirect route via synthesis gas (syngas), i.e., methane is first converted to syngas before it is further transformed into other useful products [6]. However, the production of syngas from methane is an energy intensive process. Alternative indirect pathways include conversion of methane to monosubstituted methyl halides by oxyhydrohalogenation processes over supported metal halide catalysts (Eq. 1) [7, 8] and subsequent conversion of methyl halides into useful chemicals and hydrogen halides over secondary catalysts (Eq. 2). The hydrogen halides produced are separated and recycled back to the oxidative halogenation process (Eq. 1). Methyl chloride or methyl bromide can also be produced by the selective monohalogenation of methane over supported super-acids or platinum metal catalysts [9]. Then a hydrolysis process over γ -alumina-supported metal-oxide/hydroxide catalysts converts methyl halides to mixtures of methanol and dimethyl ether [9]. Lorkovic et al. [10] have developed an integrated multi-step process where methane is converted to hydrocarbons over CaO/zeolite composites by using bromine as the mediator.



Note: X is halide

Acetic acid is the major source of commercially important materials like vinyl acetate monomer (VAM), cellulose acetate, and acetate esters. More importantly, it can be used as the solvent for many industrial processes such as the production of polyethylene terephthalate (PET) [11]. Nowadays more than 60% of the industrial production of acetic acid is obtained by the carbonylation of methanol

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[12], which is produced from syngas feedstock with Cu/ZnO/Al₂O₃ catalysts at 220–300 °C and 5–10 MPa [13]. It has been reported that methyl bromide can be carbonylated by carbon monoxide over rhodium-based catalyst to produce acetic acid [14]. The possibility of acetic acid production using carbonylation of methyl chloride has been discussed [15], although it was believed to be not easily realized [16, 17]. However, methyl chloride is cheaper than methyl bromide and its prospective use becomes more attractive if it can be coupled with the recent breakthrough by Dow Chemical scientists, who reported new and more efficient routes for the production of methyl chloride from the oxyhydrochlorination of methane over a lanthanum catalyst [18]. Therefore, it is desired to develop a catalytic system for the carbonylation of methyl chloride to produce acetic acid. In this paper, we report the carbonylation of methyl chloride with carbon monoxide over metal salt catalysts. The role of the catalysts and the mechanism are discussed.

2 Experimental

The carbonylation of chloride methane was carried out in a pressurized batch reactor, which was a tailor-made stainless steel autoclave lined with polytetrafluoroethylene with an inner volume of about 2.0 mL. The catalyst, promoters (when used) and the solvent (propionic acid, 0.4 mL) were preloaded and sealed in the reactor. Subsequently, about 0.6 mmol chloride methane gas was introduced into the reactor. Then, the reactor was pressurized to a specified pressure with carbon monoxide, and heated to the desired reaction temperature in an oil bath under magnetic stirring. After a set reaction time, the reactor was cooled down to room temperature and unsealed. About 1.5 mL deionized water was immediately added for the hydrolyzation of acetyl chloride to produce acetic acid. The resulting solution was diluted with deionized water and filtered. The products were detected by GC/MS (Agilent 6890-5973N) and quantified using a gas chromatogram (Agilent 6890N, HP-PLOT Q capillary column with a FID detector) by comparison with standard samples.

3 Results and Discussion

3.1 Selection of Catalyst and Promoters

First, seven transition metal compounds were tested as the catalyst. The corresponding catalytic activities are listed in Table 1. It can be seen that all the catalysts without promoters showed low activity in methyl chloride carbonylation. The yield of acetic acid was less than 10%. However,

when PPh₃ and/or KI were added as promoters, the yield of acetic acid increased remarkably. For example, the yield of acetic acid over the H₂IrCl₆ catalyst was 7.1% without the promoters, while it increased to 23.1% in the presence of PPh₃ and KI. Significantly, a 73.4% of acetic acid yield was obtained over the RhCl₃ catalysts. Keeping other conditions unchanged, the yield of acetic acid using KI or PPh₃ alone was 56.8% and 51.3%, respectively, showing that the individual KI or PPh₃ is not as efficient as the combination of KI and PPh₃ as promoters (Table 1, columns 2 and 3). The control experiment without using a metal salt but with PPh₃ and KI showed that the yield of acetic acid was only 2.4%, demonstrating the importance of precious metal catalysts (the main catalyst). These observations indicated that there was a synergism between the main catalyst and promoters, which ensures the outstanding catalytic performance in the carbonylation of methyl chloride. In addition, a high selectivity (about 99%) was always obtained over the catalysts with or without promoters. In the following experiments for the optimization of the reaction conditions, only the most efficient catalyst, RhCl₃ with promoters, was investigated.

3.2 Effect of Reaction Temperature

Keeping the other reactions parameters unchanged, the effect of reaction temperature on the yield of acetic acid was examined (Fig. 1). It is clear from Fig. 1 that a

Table 1 The screening of catalysts

Catalyst	Metal salt amount (mmol)	PPh ₃ (mg)	KI (mg)	Yield (%)
RhCl ₃	0.019	0	0	1.0
RhCl ₃	0.019	0	39.9	56.8
RhCl ₃	0.019	20.0	0	51.3
RhCl ₃	0.019	20.0	39.9	73.4
–	0	20.0	40.3	2.4
H ₂ IrCl ₆	0.020	0	0	7.1
H ₂ IrCl ₆	0.020	19.8	39.9	23.1
PdCl ₂	0.020	0	0	0.3
PdCl ₂	0.020	19.9	40.1	2.6
CuCl ₂	0.021	0	0	1.5
CuCl ₂	0.021	19.9	40.4	2.5
NiCl ₂	0.020	0	0	0.3
NiCl ₂	0.023	19.9	39.9	3.6
CoCl ₂	0.020	0	0	0.4
CoCl ₂	0.020	20.0	39.9	2.4
FeCl ₃	0.020	0	0	0.3
FeCl ₃	0.020	20.2	40.5	1.8

Propionic acid: 0.4 mL, chloride methane: 0.6 mmol, reaction temperature: 160 °C, CO pressure: 2.5 MPa, reaction time: 8 h

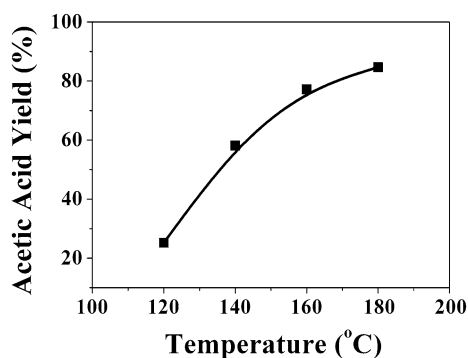


Fig. 1 Yield of acetic acid versus reaction temperature (8 h; 0.019 mmol of RhCl_3 , 20 mg of KI, 40 mg of PPh_3 , and 3 MPa of CO)

temperature dependent activity of $\text{RhCl}_3/\text{PPh}_3/\text{KI}$ system was observed. An acetic acid yield of 25.2% was obtained at the relatively low reaction temperature of 120 °C within 8 h of reaction. The yield increased with the reaction temperature and reached 84.7% at 180 °C. Experiment at higher reaction temperature was not carried out. As a matter of fact, Luft and Schrod [19] have reported that the active rhodium species would be reduced to metal and the activity of catalysts would decrease with reaction temperatures higher than 200 °C in a similar catalytic system, the synthesis of acetic anhydride from the carbonylation of methyl acetate over a rhodium catalyst. Therefore, we believe similar phenomenon would be resulted in the reaction temperature of current system is higher than 200 °C.

3.3 Effect of Initial Carbon Monoxide Pressure

The carbonylation of chloride methane is insensitive to the initial pressure of carbon monoxide in the batch reactor if the mole ratio of carbon monoxide to chloride methane is bigger than one. Figure 2 shows the relationship between the yield of acetic acid and the initial pressure of carbon

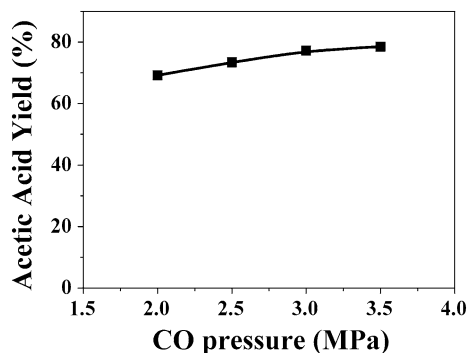


Fig. 2 Yield of acetic acid after 8 h carbonylation reaction at 160 °C versus initial CO pressure (0.019 mmol of RhCl_3 , 20 mg of KI, and 40 mg of PPh_3)

monoxide at the reaction temperature of 160 °C. When the initial pressure of CO was 2 MPa, the yield of acetic acid was 69.2%. It increased slowly with the multiplying of carbon monoxide pressure. Specifically, the acetic acid yield only changed from 69.2% to 78.5% with the carbon monoxide pressure increased from 2 to 3.5 MPa. It is clear that a 70% acetic acid yield can be reached at a relatively low initial CO pressure (2 MPa), while, in contrast, a pressure of at least 5 MPa was required in the conventional methanol synthesis from syngas developed by the ICI Co. Ltd. [20]. This suggests that an acetic acid production by the current chloride methane carbonylation approach could be better/more efficient in terms of CO utilization.

3.4 Effect of Reaction Time

The carbonylation reaction as a function of time at 160 °C and 3 MPa of carbon monoxide pressure was also investigated (Fig. 3). During the first 2 h, there was a near linear increase for the yield of acetic acid. In the next 6 h, although the acetic acid yield still increases, the reaction rate slowed down. Significantly, an acetic acid yield of 77.2% was obtained at 8 h. The yield of acetic acid leveled off after reaction time longer than 8 h. It was reported that there is an induction period in bromide methane carbonylation reaction over a rhodium catalyst, but the induction period can be eliminated by the addition of a sufficient amount of phosphine [14]. In our experiment, no obvious induction time was observed, possibly implies that the amount of phosphine and iodide promoters used in our system was sufficient.

3.5 General Discussion

It is generally accepted that in methanol carbonylation over rhodium and iridium catalysts with the promotion of iodide ions, the formation of methyl iodide, derived from methanol and iodide ions, initiates the carbonylation cycle. This

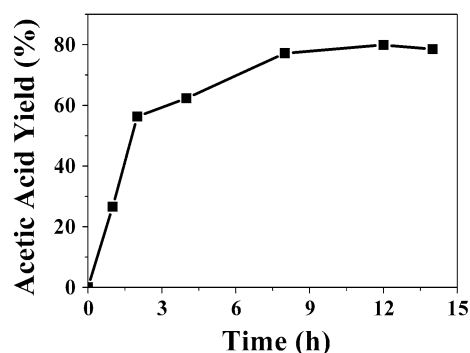


Fig. 3 Yield of acetic acid versus reaction time at 160 °C and 3 MPa of CO (0.019 mmol of RhCl_3 , 20 mg of KI, and 40 mg of PPh_3)

is a multistep process that includes oxidative addition, ligand migration, carbon monoxide insertion, and reductive elimination [21]. Similarly, chloride methane and KI in the current reaction system may be converted to methyl iodide by Cl–I exchange [22], and the methyl iodide generated then may participate in the multistep carbonylation cycle and give acetic acid as the final product. It is believed that the rate determining steps were different in the rhodium and iridium catalytic processes. For carbonylation cycle driven by rhodium catalyst, the slowest step is the oxidative addition of methyl iodide to $[\text{Rh}(\text{CO})_2\text{I}_2]^{-1}$ to generate a rhodium–methyl complex [23] and this slow oxidative addition step can be accelerated by increasing the electron density at the metal center by coordination of basic ligands, such as phosphines [24]. This is in good agree with current observation, strongly indicating that the carbonylation of chloride methane over rhodium catalyst following similar mechanism with the methanol carbonylation reaction. Moreover, for the carbonylation cycle catalyzed by iridium, the rate determining step is instead the migratory insertion of carbon monoxide.

In order to identify the role of KI, we carried out the reaction between chloride methane and KI at 160 °C for 3 h over RhCl_3 catalyst with propionic acid as solvent. Although it was difficult to quantify the extent of Cl–I exchange due to the gaseous nature of chloride methane under ambient conditions, the GC-MS result confirmed the presence of iodide methane in the resultant solution. This result showed that possibly chloride methane and KI may first undergo Cl–I exchange to form iodide methane over RhCl_3 , and then iodide methane could be carbonylated to acetic acid. It is well known that PPh_3 is a good p-electron donor, whose coordination ability to Rh is stronger than that of Cl^- or I^- . The presence of PPh_3 could accelerate the slow oxidative addition step of chloride methane on rhodium center by increasing the electron density at the metal center in the presence of PPh_3 , thus speeded the production of acetic acid [14].

The M–C bonds of 5d elements are easier to form and stronger than those of the corresponding 4d metals [25]. The C–Cl bond in chloride methane was too strong for 4d element rhodium to break without the promotion of KI or PPh_3 , resulting an acetic acid yield of only 1.0%. The 5d metal iridium showed better catalytic performance under similar conditions and the acetic acid yield was 7.1% without promoters. Although the catalytic efficiency of iridium was slightly higher than that of rhodium without promoters, it was much lower than that of rhodium after promotion with PPh_3 and KI. As we mentioned above, the slow rate-determining oxidative addition step in the carbonylation cycle over a rhodium catalyst could be enhanced by the promotion of KI and PPh_3 and the acetic acid yield reached 73.4%, whereas possibly these

promoters were not efficient for the migratory insertion steps of carbon monoxide in the carbonylation cycle catalyzed by iridium, and thus leading to an inferior reaction performance.

In the early commercialized methanol-to-acetic acid carbonylation process, nickel or cobalt carbonyl was used as catalyst [26]. As metal carbonyls, which were formed only at high carbon monoxide pressure, are supposed to be the active center for the carbonylation of methanol, a high pressure (60 MPa) and high temperature (230 °C) were usually required in this system to get a high yield of acetic acid [27]. Meanwhile, although the carbonylation of methanol to methyl acetate catalyzed by palladium has been reported, a high turnover frequency can only be achieved by using quaternary ammonium iodide and phosphine as additives [28]. The absence of these co-ligands leads to a quick deactivation of the catalyst with the formation of (inactive) palladium metal. In present case, the formation of black palladium precipitation was observed after reaction, showing that KI and PPh_3 used in our system could not stabilize the palladium catalyst and thus a low acetic acid yield was obtained. Instead, rhodium-based catalyst is stable through out the reaction process, and it gave out very high acetic acid yield at ambient conditions. Current approach, with a much lower operation temperature and pressure, opens new opportunities for the utilization of methane and the production of acetic acid, once coupling with recent developed process for CH_3Cl production.

4 Conclusions

The carbonylation of methyl chloride to produce acetic acid was realized in a metal salt/ PPh_3 /KI system at relatively low temperature and pressure. Under optimized reaction conditions, an acetic acid yield of 84.7% was reached in 8 h over a rhodium-based catalyst promoted by KI and PPh_3 . With coupling with the new methyl chloride production process recently developed by Dow Chemicals, this might give a next generation of natural gas utilization route.

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