The palladium catalyzed hydrocarboxylation of acetylene with carbon monoxide to acrylic acid under mild conditions

Cong-Ming Tang [a,b,c,d], Yi Zeng [a], Xian-Gui Yang [a], Yong-Cheng Lei [a], Gong-Ying Wang [a,c,*]

[a] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, PR China
[b] College of Chemistry and Chemical Engineering, China West Normal University, Nanchong, Sichuan 637002, PR China
[c] Changzhou Institute of Chemistry, Changzhou, Jiangshu 213164, PR China
[d] Graduate School of Chinese Academy of Sciences, Beijing 10049, PR China

ABSTRACT

Hydrocarboxylation of acetylene with carbon monoxide to acrylic acid has been carried out using a catalyst system consisting of Pd(OAc)$_2$, phosphine ligands and acids under the mild conditions. The effects of acidic promoters, phosphine ligands, water, reaction time and the initial partial pressure of carbon monoxide on the conversion of acetylene as well as the selectivity to acrylic acid have been investigated. Among all ligands as used, only diphenyl-2-pyridylphosphine has a good catalytic activity. Sulfonic acids and trifluoroacetic acid as acidic promoters display an excellent performance. Effects of water and the initial partial pressure of carbon monoxide have also been discussed. Under the optimal reaction conditions, 85% conversion of acetylene and 99% selectivity to acrylic acid as well as 1011 h^{-1} TOF have been achieved.

1. Introduction

Acrylic acid and its esters have wide industrial applications as textile and leather finishes, adhesives, and coatings, especially as monomers for polymer synthesis [1,2]. There are main two routes for the synthesis of acrylic acid at present [3,4]. One route is the partial oxidation of propene. The other route is the direct synthesis of acrylic acid by carbonylation of acetylene with carbon monoxide. Compared with the former, the latter is viewed as a potential route because the former is facing the lack of petroleum, leading to the gradual increase of its cost.

The route for synthesis of acrylic acid via carbonylation of acetylene was firstly found by Reppe in 1939. They utilized Ni(CO)$_4$ as a catalyst to catalyze acetylene, carbon monoxide and water to acrylic acid in the presence of hydrochloric acid. Since Ni(CO)$_4$ is highly poisonous, its commercial application as a catalyst must be limited and substituted by other catalysts [3,5]. An exhaustive and intensive study was made by Bhattacharyya and coworkers, using salts of iron, cobalt, and nickel as catalysts [2,6,7]. But under optimal conditions, the conversion of acetylene to acrylic acid was low, only 14.2% using nickel naphthenate catalyst. In the subsequent work on carbonylation of acetylene, nickel bromide catalyst system was reported by Yize An [8,9]. The catalyst system was demonstrated to catalyze the carbonylation of acetylene with high conversion under high carbon monoxide pressure at high temperature. More recently, we have reported nickel acetate system with the conversion of 90% and the selectivity of 90% for hydrocarboxylation of acetylene with carbon monoxide to acrylic acid [10]. Although the above nickel catalytic systems displayed an excellent performance, they must require severe reaction conditions, i.e. the reaction temperature of at least 200 °C and the reaction pressure of at least 8.0 MPa; otherwise, no reaction was observed or the rate of reaction became very slow.

However, under mild conditions, the catalysts with an excellent catalytic performance attract more and more attention [11–15]. It is well known that palladium catalysts are able to display a good catalytic activity under mild conditions. Palladium catalyst systems with different ligands such as Pd(PPh$_3$)$_4$, Pd(OAc)$_2$/dppf [16], Pd(OAc)$_2$/dppb/PPh$_3$ [17] and Pd(dba)$_2$/PPh$_3$ [18] have been demonstrated to catalyze the carbonylation of terminal or internal alkynes at low CO pressures. But in all above cases, the reaction rates were lower and relative higher selectivities for terminal alkynes than that for internal alkynes were observed. Subsequently, most of works focus on the activity of the palladium catalysts.

* Corresponding author at: Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, PR China. Tel.: +86 28 85250005; fax: +86 28 85220713.
E-mail address: gywang@cioc.ac.cn (G.-Y. Wang).

A case is that a novel palladium complex catalyst consisting of $Pd(OAc)_2/PPh_3/pyca/p$-tsa for hydroesterification of alkynes with high activity (TOF, 3500 h^{-1}) and high selectivity (98%) was developed by Jayasree et al. [1]. Another case is that a catalyst system consisting of $Pd(OAc)_2/2$-PyPPh$_2$ was used for hydroesterification of propyne with higher catalytic activity (40,000 h^{-1}) and higher selectivity (99.95%) under 6.0 MPa CO pressure at the temperature of 50–80 °C [19].

Although the palladium catalyzed hydroesterification of alkynes has been investigated much more in the past decades years, the investigation about the palladium catalyzed hydrocarboxylation of alkynes with carbon monoxide and water as nucleophilic reagent to olefine acid, especially for acetylene, is very rare. Beshouri and Garcia [20] have reported palladium catalysts active for carbonylation of acetylene with carbon monoxide to acrylic acid below 80 °C under 6.0 MPa. However, the knowledge on the use of this catalyst system for hydrocarboxylation is still quite limited. Thus this prompted us to further research on the catalyst system. In this paper, the effects of various parameters such as acidic promoters, anion to catalyst ratio, ligand to metal ratio, water amount, initial partial pressure of carbon monoxide, reaction time on the catalytic activity and product selectivity are reported.

2. Experimental

2.1. Materials

Palladium(II) acetate, diphenyl-2-pyridylphosphine (2-PyPPh$_2$, 97%), trifluoromethane sulfonic acid, methanesulfonic acid, trifluoroacetic acid, p-toluenesulfonic acid monohydrate, PPh$_3$, tris(3-sulfonatophenyl)phosphine sodium (TPPTS), tert-butyldiphenylphosphine, benzyldiphenylphosphine, allyldiphenylphosphine (all from Aldrich, USA) were used as supplied. Acetylic acid, hydrochloric acid, acetylene and carbon monoxide were purchased from commercial sources and were used for the carbonylation reaction without further purification.

2.2. General procedure

Both liquid samples and gas samples were analyzed on a SC-2000 Series GC, which is controlled by the N2000 Chemstation software, by using a packed column (2.6 m × 2 mm, on a poly(ethylene glycol) stationary phase). The carbonylation reactions were carried out in a 250 ml autoclave made of stainless steel – 316 having facilities for gas inlet, outlet, temperature controlled heating and variable agitation speed. In a typical reaction, palladium(II) acetate (5.0×10^{-2} mmol), diphenyl-2-pyridylphosphine (1.5 mmol) and trifluoromethane sulfonic acid (3.3 mmol) were dissolved in a mixture of 50 ml acetone and 12 ml (667 mmol) water and charged to the reactor. The reactor was firstly purged several times with nitrogen and subsequently pressurized with acetylene

and to 0.1 MPa (62 mmol C_2H_2), and to 1.1 MPa with CO at room temperature. The reactants were heated up to 50 °C in water bath within 5 min. The reaction proceeded at 50 °C for 60 min, then the reaction system was cooled to room temperature. The gas samples and the liquid samples were immediately analyzed by gas chromatography and GC–MS.

Conversion of acetylene and selectivity to acrylic acid or byproducts are defined as follows:

$$\text{conversion}(\%) = \frac{n_0 - n_1}{n_0} \times 100, \ \text{selectivity}(\%) = \frac{n_p}{n_0 - n_1} \times 100$$

where n_0 is the amount of acetylene for input before reaction, n_1, the amount of acetylene for residue after reaction and n_p, the amount of acetylene for formation of acrylic acid or byproducts.

3. Results and discussion

3.1. Effect of different acidic promoters

The effect of different acidic promoters is given in Table 1. The conversion of acetylene, and TOF decreases in the order trifluoromethane sulfonic acid, methanesulfonic acid, trifluoroacetic acid, p-toluenesulfonic acid, hydrochloric acid, acrylic acid, acetic acid, which almost accords with the order of acid strength of these acids with the exception of hydrochloric acid. Higher activities are observed with sulfonic acids and trifluoroacetic acid under the experimental conditions. Although trifluoroacetic acid has a lower catalytic activity for hydroesterification of styrene [21], it displays a good activity for hydrocarboxylation of acetylene. The difference may be caused by the different molecular structures between alkene and alkyne. However the highest conversion (85%) is obtained in the case of trifluoromethane sulfonic acid. The lowest performances are observed in the presence of acetic acid and acrylic acid, respectively. We had intended to utilize acrylic acid as a acid promoter to improve the performance of the catalyst. Unfortunately, the catalyst has no activity under the experimental conditions whether the molar ratio of acrylic acid/Pd is 100 or 300. Although hydrochloric acid is very strong in acidity, reactivity and selectivity are relative lower. The possible reason is that chloric anion strongly coordinates toward the centre of palladium which results in decrease in the coordination of other molecules such as carbon monoxide, acetylene, water and 2-PyPPh$_2$ [19]. Therefore, it is concluded that both acidic and coordinative properties play an important role in the catalytic performance for the hydrocarboxylation of acetylene with carbon monoxide to acrylic acid.

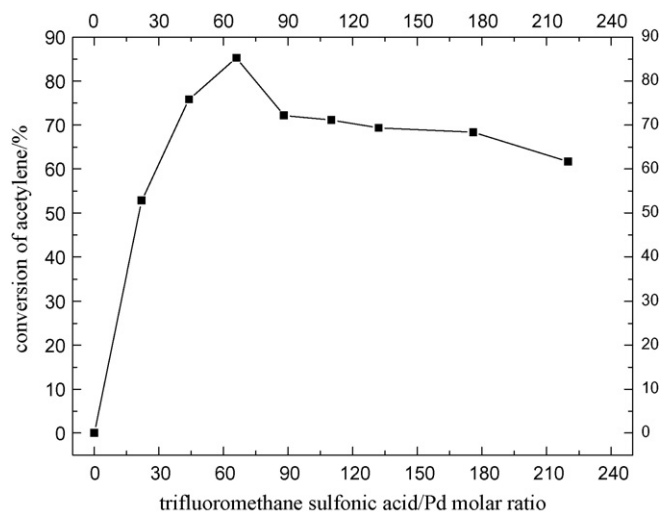### 3.2. Effect of trifluoromethane sulfonic acid concentration

The effect of trifluoromethane sulfonic acid concentration is shown in Fig. 1. The catalytic activity is zero without trifluoromethane sulfonic acid and increases drastically with increase in

Table 1
Effect of different acidic promoters.

Acidic promoters	Conversion of acetylene (%)	Selectivity (%)			TOF (h^{-1})
		AA	PA	A	
Trifluoromethane sulfonic acid	85	99.1	0.8	0.1	1011
Methanesulfonic acid	73	99.0	0.9	0.1	868
Trifluoroacetic acid	71	98.8	0.8	0.1	844
p-Toluenesulfonic acid	70	98.9	0.8	0.1	832
Hydrochloric acid	30	96.0	0.5	3.5	357
Acetic acid	No reaction				
Acrylic acid[a]	No reaction				

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-PyPPh$_2$ 1.5 mmol, acid promoters 3.3 mmol, acetone 50 ml, H_2O 12 ml, initial partial pressure: $P(CO) = 1.0$ MPa, $P(C_2H_2) = 0.1$ MPa, reaction time: 60 min, reaction temperature: 50 °C. AA: acrylic acid, PA: 2,4-pentadienoic acid, A: acetaldehyde.

[a] Acrylic acid used with acrylic acid/Pd molar ratio 100 or 300, respectively.

Fig. 1. Effect of trifluoromethane sulfonic acid concentration. Conditions: Pd(OAc)$_2$ 5.0×10^{-2} mmol, 2-PyPPh$_2$ 1.5 mmol, acetone 50 ml, H$_2$O 12 ml, initial partial pressure: P(CO) = 1.0 MPa, P(C$_2$H$_2$) = 0.1 MPa, reaction time: 60 min, reaction temperature: 50 °C.

trifluoromethane sulfonic acid concentration, which indicates that acid is necessary for this reaction. The highest conversion of about 85% is observed as the ratio of CF$_3$SO$_3$H/Pd is increased to 66. It is worth emphasizing that the selectivity to acrylic acid maintains over 98% whether the concentration of trifluoromethane sulfonic acid is high or low. However, the catalytic activity begins with a gradual decrease with further increase in trifluoromethane sulfonic acid. The possible reasons for effect of CF$_3$SO$_3$H on the catalytic activity are as follows. In an appropriate amount of CF$_3$SO$_3$H, the formation of the active Pd complex is relatively easy, so the reactivity enhances greatly. Besides, the high reactivity with weakly coordinating anion (CF$_3$SO$_3^-$) are thought to arise, in part, from the easier access of substrate molecules acetylene, carbon monoxide and water as well as diphenyl-2-pyridylphosphine ligand to the coordination sites around the metal centre. Another factor may be the increased electrophilicity of the palladium centre, which results in lower binding energies with substrate molecules due to decreased back-donation [19]. But in excess of CF$_3$SO$_3$H, the ability of H$_2$O for displacement of CF$_3$SO$_3^-$ decreases due to the competition of CF$_3$SO$_3^-$ with H$_2$O for coordination toward the centre of Pd, causing decrease in the ability of activation for H$_2$O, thus the

catalytic activity decreases a little. In addition, under higher concentration of strong acid, the phosphine ligand may get quaternized with activated olefin product, resulting in lowering the concentration of ligand, which ultimately may result in decrease in the catalyst [1,22]. Furthermore, the phosphine ligand will be also consumed much because the pyridine group of 2-PyPPh$_2$ can react with strong acid, leading to decrease in catalyst activity.

3.3. Effect of phosphine ligands

Effect of phosphine ligands is summarized in Table 2. It is found that the molar ratio of 2-PyPPh$_2$ to Pd has a significant role in catalytic activity. No reaction is observed in the absence of 2-PyPPh$_2$. A marked increase in the activity is observed with increase in 2-PyPPh$_2$/Pd ratio from 0 to 30. With a 2-PyPPh$_2$/Pd ratio up to 30, the highest conversion of acetylene (85%) is achieved under the experimental conditions and the conversion decreases slowly with further increase in 2-PyPPh$_2$/Pd molar ratio. However the selectivity to acrylic acid is hardly affected with the change of 2-PyPPh$_2$ concentration and always maintains about 99%.

High selectivity and high catalytic reactivity can be mainly ascribed to 2-PyPPh$_2$ for activating CO and C$_2$H$_2$ molecules in the presence of 2-PyPPh$_2$ under the experimental conditions. No reactivity is observed without 2-PyPPh$_2$, which indicates that Pd^{2+} cation has no catalytic activity, but Pd complex composed of 2-PyPPh$_2$ has an excellent activity. In the appropriate concentration of 2-PyPPh$_2$ such as the 2-PyPPh$_2$/Pd molar ratio of 15–37, the active Pd phosphine complex is easily generated. But in excess of 2-PyPPh$_2$, it competes with the reactant molecules such as CO, C$_2$H$_2$ and H$_2$O for coordination toward Pd centre, causing decrease in the activity.

When a half part of 2-PyPPh$_2$ is replaced by PPh$_3$, the conversion of acetylene decreases to 53.7% (2-PyPPh$_2$ + PPh$_3$/Pd = 45), lower than that with only 2-PyPPh$_2$ (79.1%, 2-PyPPh$_2$/Pd = 15). It is known that a synergistic effect of similar ligands has been observed in a few other carbonylation reactions [1,18,17]. However the minus effect is observed in this reaction. Coordination ability of PPh$_3$ may be stronger than that of 2-PyPPh$_2$, which results in the formation of Pd–PPh$_3$, leading to decrease in the activity of the catalyst. In addition, other phosphine ligands such as PPh$_3$, TPPTS, tert-butyldiphenylphosphine, benzyldiphenylphosphine and allyldiphenylphosphine, which are used alone, have no catalytic activity for this reaction under the experimental conditions.

Table 2
Effect of phosphine ligands.

Phosphine ligands	Ligand/Pd molar ratio	Conversion of acetylene (%)	Selectivity (%)		
			AA	PA	A
2-PyPPh$_2$	4	42.6	98.9	0.9	0.1
	8	54.9	99.0	0.9	0.1
	15	79.1	99.1	0.8	0.1
	23	80.2	99.0	0.8	0.1
	30	85.2	99.1	0.7	0.1
	37	79.8	99.1	0.8	0.1
	45	77.7	99.0	0.9	0.1
	60	76.8	99.1	0.8	0.1
2-PyPPh$_2$/PPh$_3$[a]	45	53.7	99.1	0.8	0.1
PPh$_3$	No reaction				
TPPTS	No reaction				
tert-Butyldiphenylphosphine	No reaction				
Benzyldiphenylphosphine	No reaction				
Allyldiphenylphosphine	No reaction				

Conditions: Pd(OAc)$_2$ 5.0×10^{-2} mmol, CF$_3$SO$_3$H 3.3 mmol, acetone 50 ml, H$_2$O 12 ml, initial partial pressure: P(CO) = 1.0 MPa, P(C$_2$H$_2$) = 0.1 MPa, reaction time: 60 min, reaction temperature: 50 °C. AA: acrylic acid, PA: 2,4-pentadienoic acid, A: acetaldehyde.
[a] 2-PyPPh$_2$/PPh$_3$: molar ratio is 0.5.

Table 3
Effect of initial partial pressure of carbon monoxide.

Initial partial pressure of carbon monoxide (MPa)	Conversion of acetylene (%)	Selectivity to AA (%)	TOF (h^{-1})
0.7	60.8	99.1	713
1.0	85.2	99.1	1011
1.5	80.3	99.0	951
2.0	77.1	99.1	915
3.0	69.1	99.1	820
4.0	68.3	99.2	808
5.0	69.1	99.1	820

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, CF_3SO_3H 3.3 mmol, 2-PyPPh$_2$ 1.5 mmol, acetone 50 ml, H_2O 12 ml, initial partial pressure: $P(C_2H_2) = 0.1$ MPa, reaction time: 60 min, reaction temperature: 50 °C. AA: acrylic acid.

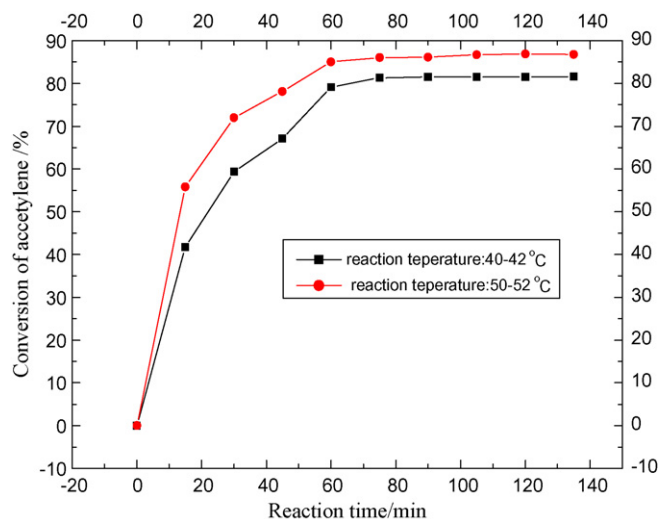### 3.4. Effect of initial partial pressure of carbon monoxide

The effect of initial partial pressure of carbon monoxide on the hydrocarboxylation of acetylene is shown in Table 3. Surprisingly, the conversion of acetylene is 85.2% under the initial partial pressure of carbon monoxide of 1.0 MPa at reaction temperature of 50 °C with the high selectivity of 99.1%. As well known to all, the nickel catalyzed carbonylation reaction of acetylene with carbon monoxide to acrylic acid required severe conditions, i.e. reaction temperature of at least 200 °C and reaction partial pressure of carbon monoxide of at least 7.5 MPa. The selectivity to acrylic acid is not affected with change of initial partial pressure of carbon monoxide from the experimental results in Table 3. But it has a strong influence on the conversion of acetylene. When initial partial pressure of carbon monoxide is 0.7 MPa, the conversion is only 60.8%. Subsequently, the conversion increases with increase in the initial partial pressure of carbon monoxide. However the conversion decreases slowly when initial partial pressure of carbon monoxide is above 1.0 MPa. It is interesting that the conversion almost remains constant when initial partial pressure of carbon monoxide is above 3.0 MPa.

3.5. Effect of H$_2$O

The effect of H$_2$O on the reaction is shown in Fig. 2. The conversion of acetylene enhances drastically with increase in H$_2$O. The highest conversion of 85% was achieved when 12 ml of H$_2$O
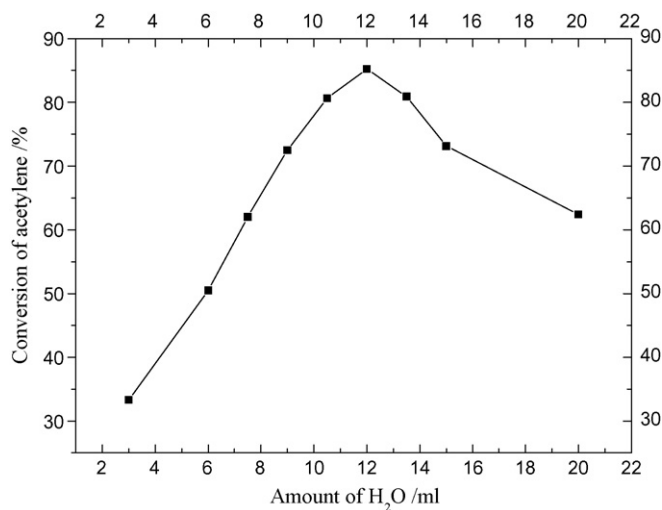
Fig. 3. Effect of reaction time. Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-PyPPh$_2$ 1.5 mmol, CF_3SO_3H 3.3 mmol, acetone 50 ml, H_2O 6 ml, initial partial pressure: $P(CO) = 1.0$ MPa, $P(C_2H_2) = 0.1$ MPa.

was used in the reaction system. However the conversion began with decrease when the amount of H$_2$O was above 12 ml. For example, the conversion decreased to about 60% in the presence of 20 ml of H$_2$O in the reaction. The possible reasons are as follows. On one hand, water can enhance the concentration of the active species Pd–H besides acids through the following reaction of CO with the formation of a species having Pd–(COOH) moiety, which upon elimination of CO$_2$ yields a Pd–H species, and the reaction is given as follows [21]. Furthermore, water also acts as a reactant, and can influence reaction rate via increasing the rate of attack of water on a Pd–acyl complex indicated in subsequent Eq. (12). Therefore, the conversion increases with an increase in water. On the other hand, the solubility of 2-PyPPh$_2$ decreases with an increase of water leading to decrease in the concentration of the active species Pd–H due to decomposition of Pd phosphine complexes, which results in the lower conversion of acetylene.
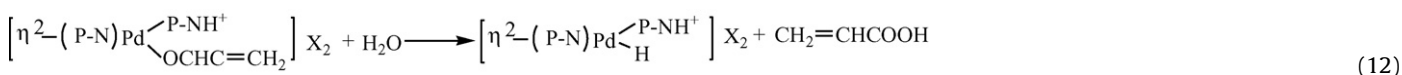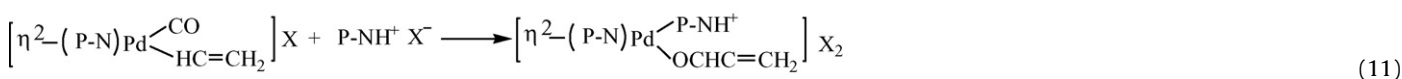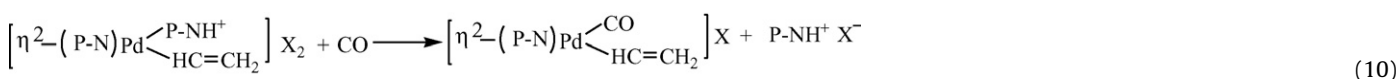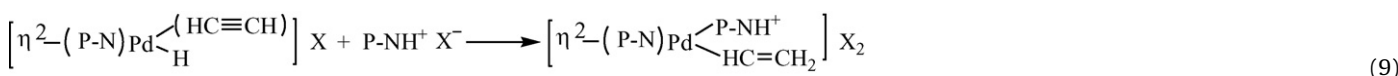
$$[L_nPd] + CO + H_2O \xrightarrow{-H^+} [L_nPd(COOH)]^+ \xrightarrow{-CO_2} [L_nPd–H]^+$$

$$L = 2\text{-PyPPh}_2, \ CF_3SO_3^- \ or \ CO; \ n = 2, \ 3 \ or \ 4$$

3.6. Effect of reaction time

Fig. 3 shows the effect of reaction time on the acetylene conversion for this reaction at about 40/50 °C. The conversion of acetylene enhances drastically from 0% to 80% within 60 min. After 60 min, the conversion of acetylene increases only a little. In addition, higher initial reaction rate was observed at higher temperature. But it is disadvantage for the catalyst at overtemperature such as 90 °C because the black palladium metal is observed due to decomposition of the catalyst. Likewise, the reaction rate is very slow at the temperature below 20 °C. Thus, we choose the reaction temperatures of 40/50 °C to check the influence of reaction time. From the experimental results, higher conversion of above 80% is obtained in 1 h for this reaction. Subsequently, the conversion almost remains constant although the reaction time is lengthened. The possible reason is that the concentration of acetylene decreases with reaction time, resulting in decrease in the coordination of acetylene toward the Pd centre due to the competition of carbon monoxide with strong coordination ability.

Fig. 2. Effect of H$_2$O. Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-PyPPh$_2$ 1.5 mmol, CF_3SO_3H 3.3 mmol, acetone 50 ml, initial partial pressure: $P(CO) = 1.0$ MPa, $P(C_2H_2) = 0.1$ MPa, reaction time: 60 min, reaction temperature: 50 °C.

3.7. Reaction mechanism

On the basis of our experiments, the following mechanisms, which are similar to the possible mechanisms presented to explain nickel or palladium catalyzed hydroesterification of methylacetylene or acetylene with carbon monoxide [3,8,19,21,23–25], may be proposed:

$$Pd(CH_3COO)_2 + 2HX \rightarrow PdX_2 + 2CH_3COOH \tag{1}$$

$$PdX_2 + 2(2\text{-}PyPPh_2) \rightarrow [\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)X]^+X \tag{2}$$

$$[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)X]^+X^- + H_2O \rightarrow [\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)OH]X + HX \tag{3}$$

$$[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)OH]X + HX \rightarrow [\eta^2\text{-}(P\text{-}N)Pd(P\text{-}NH^+)OH]X_2 \tag{4}$$

$$[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}NH^+)OH]X_2 + CO$$
$$\rightarrow [\eta^2\text{-}(P\text{-}N)Pd(CO)OH]X + P\text{-}NH^+X^- \tag{5}$$

$$[\eta^2\text{-}(P\text{-}N)Pd(CO)OH]X + P\text{-}NH^+X^-$$
$$\rightarrow [\eta^2\text{-}(P\text{-}N)Pd(P\text{-}NH^+)COOH]X_2 \tag{6}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}NH^+)COOH\right]X_2 \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\H\end{smallmatrix}\right]X_2 + CO_2 \tag{7}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\H\end{smallmatrix}\right]X_2 + HC\equiv CH \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}(HC\equiv CH)\\H\end{smallmatrix}\right]X + P\text{-}NH^+X^- \tag{8}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}(HC\equiv CH)\\H\end{smallmatrix}\right]X + P\text{-}NH^+X^- \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\HC=CH_2\end{smallmatrix}\right]X_2 \tag{9}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\HC=CH_2\end{smallmatrix}\right]X_2 + CO \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}CO\\HC=CH_2\end{smallmatrix}\right]X + P\text{-}NH^+X^- \tag{10}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}CO\\HC=CH_2\end{smallmatrix}\right]X + P\text{-}NH^+X^- \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\OCHC=CH_2\end{smallmatrix}\right]X_2 \tag{11}$$

$$\left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\OCHC=CH_2\end{smallmatrix}\right]X_2 + H_2O \longrightarrow \left[\eta^2\text{-}(P\text{-}N)Pd\begin{smallmatrix}P\text{-}NH^+\\H\end{smallmatrix}\right]X_2 + CH_2=CHCOOH \tag{12}$$

(HX = organic or inorganic acids, P–N in the structure of $[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)X]^+X^-$ symbolizes the 2-PyPPh$_2$ ligand).

Reaction (1) is that anions X of strong acids (HX) displace the acetate anion from palladium acetate via a simple acid–base reaction, thus generating cationic palladium(II) species. Reaction (2) is coordination of 2-PyPPh$_2$ toward palladium metal centre to the formation of $[\eta^2\text{-}(P\text{-}N)Pd(P\text{-}N)X]^+X^-$ followed by reactions (3)–(7), thus the catalytic active species Pd–H is formed. The cycle of catalytic reactions is composed of reactions (7)–(12).

PPh$_3$ is found to act as an excellent ligand for nickel catalyzed carbonylation of acetylene with carbon monoxide to acrylic acid in our previous investigations [10]. But no catalytic activity was observed when it was used as a ligand for palladium catalyst to catalyze this reaction. Compared with monodentate ligand of PPh$_3$, P–N bidentate ligand of 2-PyPPh$_2$ has an excellent activity due to the difference of structure between PPh$_3$ and 2-PyPPh$_2$. N atom in 2-PyPPh$_2$ will also increase the electron density of palladium centre when N atom is coordinated to Pd metal centre, causing an increase in activity.

Trifluoromethane sulfonic acid is the strongest acid among the investigated acids such as trifluoromethane sulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, chlorhydric acid, trifluoroacetic acid, acetic acid. So anion $CF_3SO_3^-$ easily displaces the acetate anion from palladium acetate via a simple acid–base reaction in reaction (1). Moreover, $CF_3SO_3^-$ has a low ability for coordination toward the centre of palladium. This favors the displacement of $CF_3SO_3^-$ by reactant molecule H$_2$O. Therefore, CF_3SO_3H displays the most excellent catalytic performance.

To a certain extent, based on our experiments, the reaction mechanism has been elucidated. Although a full elucidation of reaction mechanism about palladium catalyzed carbonylation of acetylene with CO under such mild conditions is very difficult at present, further investigations have been under way in our group.

4. Conclusions

Hydrocarboxylation of acetylene has been studied using a catalyst system which contains Pd(OAc)$_2$, phosphine ligands and acids under the CO initial partial pressure of 0.7–5.0 MPa at the temperature of 40/50 °C. The catalytic activity was found strongly influenced by acidic promoters and phosphine ligands. Although a synergistic effect of similar ligands was observed in other carbonylation reactions, the effect was not observed in this reaction. In addition, other parameters such as water and initial partial pressure of CO have also a great influence on the catalytic activity. Under the optimal experimental conditions, the catalyst system has displayed an excellent catalytic performance with 85% conversion of acetylene, 99% selectivity to acrylic acid and 1011 h^{-1} TOF.

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