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A highly efficient catalyst for direct synthesis of methyl acrylate via methoxycarbonylation of acetylene

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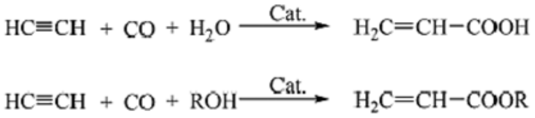
Abstract−A non-petroleum approach for the catalytic synthesis of methyl acrylate via methoxycarbonylation of acetylene with carbon monoxide and methanol as nucleophilic reagent has been studied under various conditions. $Pd(OAc)_2$/2-$PyPPh_2$/p-tsa was found to be a highly efficient catalytic system. The types of phosphorus ligands and their concentration was a determinative factor for catalytic activity. Mono-dentate phosphorus ligand such as triphenylphosphine has no activity while 2-(diphenylphosphino)pyridine with a mixed N-P bidentate structure has an excellent activity. Catalytic performance of acids depends on their acidic strength and coordinative property. Among all acidic promoters, *p*-toluenesulfonic acid displayed an excellent performance. Other parameters such as solvent polarity and initial pressure of carbon monoxide have also important influences on the hydroesterification of acetylene. It is beneficial for the reaction that the solvents have a high polarity. At low pressure of carbon monoxide, to high active palladium catalyst, the reaction easily proceeded. However, at high pressure of carbon monoxide, acetylene will transfer from solution to gas phase, resulting in lower conversion of acetylene. In addition, due to steric hindrance of alcohols, methanol has a highest activity in hydroesterification of acetylene in low carbon alcohols. Under the optimal reaction conditions, 99.5% of acetylene conversion and 99.7% of selectivity toward methyl acrylate as well as 2,502 h^{-1} TOF were achieved.

Key words: Palladium Acetate, N-P Ligands, Methoxycarbonylation, Methyl Aacrylate, Acetylene

INTRODUCTION

As one of the most important bulk chemicals, acrylic esters are synthesized via esterification of acrylic acid with alcohols [1]. At present, acrylic acid is produced by the partial oxidation of propene from petroleum. Since the petroleum resource is gradually decreasing, the non-petroleum approach for commercial production of bulk chemicals plays an important role in the chemical industry. In all non-petroleum paths, acetylene carbonylation is especially important. On one hand, the natural gas ultimate recoverable reserves are about 327.4×10^{12} m^3, and unconventional gas resources are about 1,390×10^{12}~4,430×10^{12} m^3. The total amount of natural gas is at least three times that of petroleum. On the other hand, acetylene is very easily obtained from thermal cracking of natural gas. Therefore, in the future, the path for acrylic acid based on acetylene carbonylation has rich raw material. Furthermore, the carbonylation reaction of acetylene has an ideal atom economy, which has been widely thought to be a highly promising and eco-friendly route for synthesis of α, β-unsaturated carboxylic acids or esters [2-5], and the reaction is given in Scheme 1.



$$HC{\equiv}CH + CO + H_2O \xrightarrow{Cat.} H_2C{=}CH{-}COOH$$

$$HC{\equiv}CH + CO + ROH \xrightarrow{Cat.} H_2C{=}CH{-}COOR$$

Scheme 1. Catalyzed carbonylation of acetylene with carbon monoxide to acrylates or acrylic acid.

Since Reppe et al. [6] first utilized nickel carbonyl catalyst to catalyze acetylene, carbon monoxide and water to acrylic acid in the presence of halide promoters, many nickel catalysts have been developed in carbonylation of alkynes. Sakakibara et al. used nickel carbonyl to catalyze the carbonylation reaction of methylacetylene with the total yield (46%) of methyl methacrylate and methacrylic acid at 170-180 °C [7,8]. Bhattacharyya et al. [9-11] made exhaustive and intensive studies on carbonylation of acetylene with carbon monoxide to acrylic acid or esters. But under the optimal conditions, acrylic acid yield was obtained at 14.2% using nickel naphthenate catalyst; methyl acrylate, ethyl acrylate, n-butyl acrylate yields were obtained 47.3%, 61.3%, 80.3%, respectively, using nickel iodide supported on the silica gel. In another work, synthesis of acrylic acid via carbonylation of acetylene using nickel bromide catalyst system was reported by An et al. [12]. Yang et al. developed $Ni(OAc)_2$/$CuSO_4$/NaI system for hydroesterification of acetylene with methyl formate to methyl acrylate [13]. Under the optimal reaction conditions, 64% of methyl formate conversion and 86% of methyl acrylate selectivity were achieved. Recently, we reported $Ni(OAc)_2$/$CuBr_2$/PPh_3 system with 90% of acetylene conversion and 90% of selectivity for the hydrocarboxylation reaction of acetylene with carbon monoxide to acrylic acid [14]. Although the nickel catalytic systems displayed an acceptable performance for carbonylation of alkynes, catalytic reaction can occur only under high temperature and high pressure; otherwise, no reaction was observed or the reaction velocity

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became very slow.

Compared with nickel catalysts, palladium catalysts have high activities in many reactions under mild conditions [15-22]. Palladium systems such as $Pd(PPh_3)_4$, $Pd(OAc)_2$/dppf, $Pd(OAc)_2$/dppb/PPh_3, $Pd(dba)_2/PPh_3$ have been demonstrated to catalyze the carbonylation of alkynes at low carbon monoxide pressures [23-25]. But in all the above cases, the reaction rates were lower. Subsequently, most of the works have focused on the activity of the palladium catalysts. Jayasree et al. developed a palladium complex catalyst consisting of $Pd(OAc)_2/PPh_3$/pyca/p-tsa for hydroesterification of alkynes with high activity (TOF, 3,500 h^{-1}) and high selectivity (98%) [5]. 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 and higher selectivity under 6.0 MPa carbon monoxide pressure at the temperature of 50-80 °C [26,27]. Recently, we reported that palladium catalyst can efficiently catalyze hydrocarboxylation of acetylene with carbon monoxide to acrylic acid with 85% of acetylene conversion and 99% of selectivity [28].

Knifton et al. reported palladium catalysts active for carbonylation of acetylene with carbon monoxide to methyl acrylate [29]. However, the knowledge on the use of this catalyst system for hydroesterification is still quite limited. Thus this encouraged us to further research the catalyst system. The aim of this work is to discuss the relationship between the catalytic performance and catalyst component in order to develop an efficient class of palladium catalyst for production of acrylates from carbonylation of acetylene. Various parameters such as acidic promoters, anion to metal ratio, ligand to metal ratio, alcohols, solvents, initial partial pressure of carbon monoxide on the catalytic activity and selectivity have been carefully investigated. Compared with hydrocarboxylation of acetylene previously reported by us, palladium catalyst was found to be more efficient for methoxycarbonylation of acetylene with carbon monoxide to methyl acrylate.

EXPERIMENTAL

1. Materials

Palladium(II) acetate, palladium chloride, diphenyl-2-pyridylphosphine (2-$PyPPh_2$, 97%), trifluoromethane sulfonic acid, methanesulfonic acid, trifluoroacetic acid, *p*-toluenesulfonic acid monohydrate (p-tsa), PPh_3, tris(3-sulfonatophenyl)phosphine sodium (TPPTS) (all from Aldrich, USA) were used as supplied. Acetic acid, hydrochloric acid, sulfuric acid, acetone, toluene, n-hexane, methanol, acetylene and carbon monoxide were purchased from commercial sources and were used for the carbonylation reaction without further purification.

2. Carbonylation Reaction and Analysis

The carbonylation reactions were carried out in a 250 ml autoclave made of stainless steel –316 L, following a procedure similar to that described previously [28]. In a typical reaction, Palladium(II) acetate (5.0×10^{-2} mmol), diphenyl-2-pyridylphosphine (1.51 mmol) and *p*-toluenesulfonic acid monohydrate (1.1 mmol) were dissolved in a mixture of 50 ml acetone and 12 ml methanol and charged to the reactor. The reactor was first purged thrice with N_2 and subsequently pressurized with C_2H_2 and to 0.1 MPa, and to 1.1 MPa with CO at room temperature. The contents 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 SC-2000 Series gas chromatography, which was controlled by the N2000 Chemstation software. A packed column (2.6 m×2 mm, Silicone DC-550 : GDX-102=15 : 100) was chosen for liquid samples and the other packed column (1.0 m×2 mm, TDX-01) was chosen for gas samples. The products were identified by comparison with au-

Table 1. Effect of phosphorus ligands

Entry	Phosphorus ligands	Reaction time/min	Ligand/Pd molar ratio	Conversion of acetylene/%	Selectivity/%		TOF/h^{-1}
					MA	AA	
1	2-$PyPPh_2$	30	4	60.2	99.6	0.4	3534
2		30	8	72.7	99.7	0.3	4267
3		40	16	93.4	99.6	0.4	4111
4		40	24	94.6	99.7	0.3	4163
5		60	32	99.5	99.7	0.3	2502
6		80	48	35.8	99.7	0.3	787
7		80	64	21.6	99.7	0.3	474
8	PPh_3	540	32	Trace			
9	PPh_3[a]	270	16	Trace			
10	PPh_3[b]	270	16	Trace			
11	PPh_3[c]	180	16	Trace			
12	PPh_3[d]	180	16	Trace			
13	TPPTS	540	32	No reaction			

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, *p*-toluenesulfonic acid 1.1 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, P(C_2H_2)=0.1 MPa, reaction temperature: 50 °C, MA: methyl acrylate, AA: acrylic acid

[a] Addition of 0.80 mmol pyridine

[b] Addition of 0.80 mmol 2-chloropyridine

[c] Addition of 0.40 mmol pyca (2-pyridine carboxylic acid)

[d] Addition of 0.40 mmol pypca (2-piperidine carboxylic acid)

thentic materials. GC-MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment.

The conversion of acetylene and the selectivity to methyl acrylate were calculated as follows:

$$\text{Conversion}/\% = \frac{n_0 - n_1}{n_0} \times 100, \quad \text{Selectivity}/\% = \frac{n_p}{n_0 - n_1} \times 100$$

where, n_0, amount of acetylene fed before reaction, n_1, amount of acetylene for residue after reaction, n_p, amount of acetylene converted to methyl acrylate or other products.

RESULTS AND DISCUSSION

1. Effect of Ligands

From the literature it was found that phosphorus ligands are crucial for hydroesterification of unsaturated hydrocarbons [2,15,26,30,31]. We first probed the effect of phosphorus ligands on their activity and selectivity, and the results are given in Table 1. Except for 2-$PyPPh_2$, other ligands have no activity in our experiments. It is well known that TPPTS and PPh_3 have shown an excellent activity in hydroformylation catalyzed by Rh [32,33]. In hydroesterification of styrene [30], PPh_3 was used as a ligand to coordinate toward palladium(II), forming an active $Pd(OTs)_2(PPh_3)_2$ complex. Although a single PPh_3 has low activity in hydroesterification of phenylacetylene, PPh_3 combining with 2-pyridine carboxylic acid or 2-piperidine carboxylic acid displayed an excellent activity. Unfortunately, this synergistic effect was not observed in hydroesterification of acetylene. Among all ligands, 2-$PyPPh_2$ had a high activity. This reasonably led us believe that pyridyl group in 2-$PyPPh_2$ plays a crucial role. To check the effect of pyridyl group, PPh_3 alone and PPh_3 combined with pyridine or 2-chloropyridine were investigated from entries 8-10 in Table 1. Only a trace of methyl acrylate was detected by gas chromatograph. These results indicate that PPh_3 or pyridine alone has hardly any activity, but N-P mixed bidentate ligands such as 2-$PyPPh_2$ containing a phosphorus atom as well as a pyridyl group have an excellent activity [26].

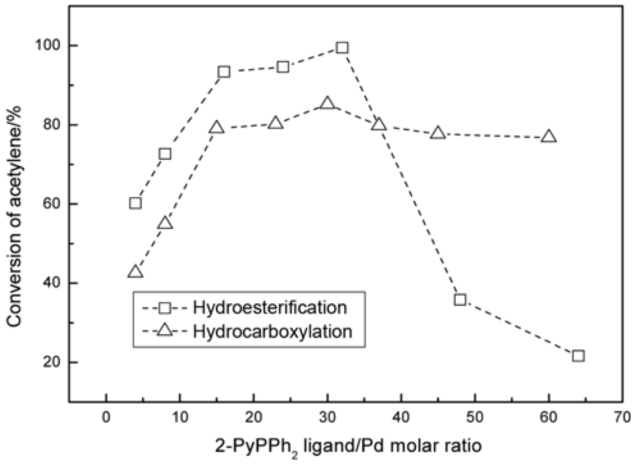


Fig. 1. Comparison between hydroesterification and hydrocaboxylation of acetylene. Conditions: in hydroesterification of acetylene to methyl acrylate, $Pd(OAc)_2$ 5.0×10^{-2} mmol, *p*-toluenesulfonic acid 1.1 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time 60 min; in hydrocarboxylation of acetylene to acrylic acid, $Pd(OAc)_2$ 5.0×10^{-2} mmol, CF_3SO_3H 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.

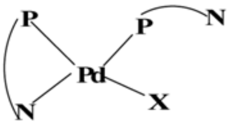


Fig. 2. Structure of active catalytic species. N-P represents 2-$PyPPh_2$ ligand, X represents acidic anion.

Subsequently, detailed experiments were performed and the results are also presented in Table 1, entries 1-7 and Fig. 1. A marked increase in the activity was observed with increase of 2-$PyPPh_2$/Pd ratio from 4 to 16. However, the further increase in 2-$PyPPh_2$/Pd molar ratio from 16 to 32, the activity slightly increased. With a 2-$PyPPh_2$/Pd ratio up to 32, the highest conversion of acetylene (99.5%) was achieved and the conversion decreased drastically with further increase in 2-$PyPPh_2$/Pd molar ratio. Although the conversion of acetylene was greatly influenced by change of 2-$PyPPh_2$ concentration, the selectivity toward methyl acrylate was hardly affected and always maintained above 99%. Besides, reaction velocity increased with an increase of 2-$PyPPh_2$ amount in low 2-$PyPPh_2$ concentration range as Table 1, entry 1 (TOF 3,534 h^{-1}, Ligand/Pd ratio 4), entry 2 (TOF 4,267 h^{-1}, Ligand/Pd ratio 8), and the reverse result was observed in high 2-$PyPPh_2$ concentration, as Table 1, entries 4-7. In hydroesterification of propyne to methyl methacrylate [26], active catalytic species was believed to be such structure given in Fig. 2. In the palladium complex, one of ligand molecules is chelating palladium(II) with both the phosphorus and the nitrogen atom creating a four-membered ring structure, while the second is mono-coordinated via the phosphorus atom only. If the concentration of 2-$PyPPh_2$ is higher, it will coordinate toward palladium(II) with a phosphorus atom forming a mono-dentate complex. However, the mono-dentate complex has no catalytic activity. Compared with our previous studies, it is evident that influence of rich phosphorus ligand atmosphere on hydroesterification of acetylene is much more than on hydrocarboxylation of acetylene (seen in Fig. 1). For example, in high concentration of the phosphorus ligand, acetylene conversion is more than 70% for hydrocarboxylation, while it is lower, around 20% for hydroesterification. These great differences may be ascribed to the reaction system. The former has rich water in which nucleophilic addition of the phosphorus ligand on acrylic acid easily occurred in the presence of strong acid, leading to decrease of phosphorus ligand [34]. However, the latter has poor water, and a similar reaction occurred with difficulty.

2. Effect of Acidic Promoters

Since the hydroesterification reaction proceeds only in the presence of acid, it is necessary to estimate the effect of different acidic promoters for their activity and selectivity. For this purpose, various acid promoters were screened, and the results given in Table 2. The conversion of acetylene decreased in the order *p*-toluenesulfonic acid, methanesulfonic acid, trifluoroacetic acid, sulfuric acid, trifluoromethane sulfonic acid, hydrochloric acid, *p*-aminobenzenesulfonic acid, acetic acid. From effect of sulfonic acid series on this reac-

Table 2. Effect of acidic promoters

Acidic promoters	Conversion of acetylene/%	Selectivity/%		TOF/h^{-1}
		MA	AA	
p-Toluenesulfonic acid	85.6	99.7	0.3	2152
Methanesulfonic acid	68.4	99.6	0.4	1720
Trifluoroacetic acid	60.0	99.2	0.8	1509
Sulfuric acid	51.8	99.3	0.7	1302
Trifluoromethane sulfonic acid	37.7	99.5	0.5	948
Hydrochloric acid	15.0	99.2	0.8	377
Hydrochloric acid[a]	13.8	99.2	0.8	347
p-Aminobenzenesulfonic acid	No reaction			
Acetic acid	No reaction			

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, acid promoters 2.2 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time: 60 min, MA: methyl acrylate, AA: acrylic acid
[a] Palladium precursor is $PdCl_2$ (5.0×10^{-2} mmol)

tion, we found that the appropriate acidic strength is a crucial factor for hydroesterification of acetylene. Although trifluoromethane sulfonic acid is an excellent acid promoter in the hydrocarboxylation reaction of acetylene [28], it displayed a low catalytic activity in the hydroesterification reaction of acetylene. Trifluoroacetic acid has a lower catalytic activity for hydroesterification of styrene [30], but it displays a good activity for hydroesterification of acetylene. The highest conversion (85.6%) was obtained in the case of *p*-toluenesulfonic acid. Surprisingly, *p*-aminobenzenesulfonic acid has no activity although it has prominent acidic property. After further search for the causes, we found that it has a poor solubility in the mixed solution composed of both acetone and methanol. This means that efficient concentration of acid was very low so that it displayed poor activity. Although hydrochloric acid is very strong in acidity, reactivity and selectivity are relatively lower. The possible reason is that chloric anion strongly coordinates toward the center of palladium, which results in decrease of coordination of other molecules such as carbon monoxide, acetylene, methanol and 2-$PyPPh_2$ [27]. Therefore, it is concluded that both acidic and coordinative properties play an important role in the catalytic performance for the methoxycarbonylation of acetylene with carbon monoxide and methanol to methyl acrylate.

3. Effect of *p*-Toluenesulfonic Acid Concentration

From the choice of acidic promoters it was found that *p*-toluenesulfonic acid was an excellent promoter. To obtain a highly catalytic performance, the effect of *p*-toluenesulfonic acid concentration on this reaction was measured and the results shown in Fig. 3. The catalytic activity was zero without *p*-toluenesulfonic acid and increased drastically with an increase in *p*-toluenesulfonic acid concentration, which indicated that acid was necessary for this reaction. The highest conversion of about 99% was obtained as the ratio of *p*-toluenesulfonic acid/Pd is increased to 22. However, the catalytic activity began with a gradual decrease with further increase of *p*-toluenesulfonic acid. The possible reasons for the effect of *p*-toluenesulfonic acid on the catalytic activity are as follows. In an appropriate amount of *p*-toluenesulfonic acid, the formation of the active Pd complex is relatively easy, so the reactivity enhances greatly. Besides, the high reactivity with weakly coordinating anion (TsO^-) is thought to arise, in part, from the easier access of substrate molecules acetylene, carbon monoxide and methanol 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 center, which results in lower binding energies with substrate molecules due to decreased back-donation [26]. But in excess of *p*-toluenesulfonic acid, the ability of methanol for displacement of TsO^- decreases due to the competition of TsO^- with methanol for coordination toward the centre of Pd, causing decrease in the ability of activation for methanol; thus the catalytic activity decreases a little. In addition, under higher concentration of strong acid, the phosphorus ligand may get quaternized with activated olefin product, resulting in lowering the concentration of ligand, which may ultimately result in the decrease of the catalyst [5,34]. Furthermore, to some extent, the phosphine ligand will be also consumed because the pyridine group of 2-$PyPPh_2$ can react with strong acid, leading to decrease of catalytic activity.

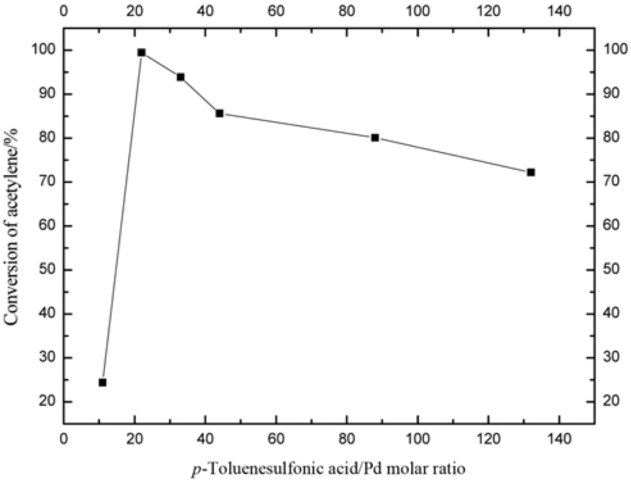


Fig. 3. Effect of *p*-toluenesulfonic acid concentration. Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time: 60 min.

4. Effect of Solvents

Due to the occurrence of hydroesterification of acetylene in solu-

Table 3. Effect of solvents

Solvents	Polarity index	Conversion of acetylene/%
Acetone	5.1	99.5
Tetrahydrofuran	4.0	71.7
Toluene	2.4	66.1
n-Hexane	0.0	36.2
Methanol	5.1	79.5

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, *p*-toluenesulfonic acid 1.1 mmol, solvent 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time: 60 min, MA: methyl acrylate, AA: acrylic acid

tion, screening ideal solvents becomes an important factor. Table 3 shows the effect of solvents on the methoxycarbonylation of acetylene with carbon monoxide and methanol to methyl acrylate. From the results, the conversion of acetylene was drastically affected by the solvents. The highest conversion (99.5%) was obtained using acetone as solvent. However, the lowest acetylene conversion (36.2%) was achieved using n-hexane as solvent. The results suggest that it is beneficial for the reaction in high polar solvents.

Besides, acetone, tetrahydrofuran and methanol displayed an excellent ability for the solubility of acetylene (seen in Table 4), and these favored transference of acetylene from gas phase to solution, resulting in high conversion of acetylene.

Table 4. The solubilities of acetylene in different solvents

Solvents	Polarity index	Viscosity/ cp, 20 °C	Boiling point/ °C	Solubility of acetylene/g
n-Hexane	0.0	0.33	69	0.8
Toluene	2.4	0.59	111	0.9
Methanol	5.1	0.60	65	1.9
Tetrahydrofuran	4.0	0.55	66	2.3
Acetone	5.1	0.32	56	2.5
Water	9.0	1.0	100	---

Conditions: Solvent 50 mL, agitation 330 r/min, time 21 min, temperature 20 °C, pressure of acetylene 0.1 MPa

Table 5. Effect of initial partial pressure of carbon monoxide

Entry	Initial partial pressure of carbon monoxide/MPa	Conversion of acetylene/%	Selectivity/%	
			MA	AA
1	0.8	99.8	99.7	0.3
2	1.0	99.5	99.7	0.3
3	1.0[a]	71.7	99.6	0.4
4	1.5	85.1	99.6	0.4
5	2.0	60.8	99.5	0.5
6	3.0	56.1	99.4	0.6

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, *p*-toluenesulfonic acid 1.1 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time: 60 min, MA: methyl acrylate, AA: acrylic acid

[a] The reaction system was pressurized to 2.4 MPa with N_2

5. Effect of Initial Partial Pressure of Carbon Monoxide

From Table 5, it is obvious that the conversion of acetylene decreased drastically with increase of initial partial pressure of carbon monoxide. The highest conversion of acetylene (99.8%) was obtained when the initial partial pressure of CO was lowest, at 0.8-1.0 MPa. However, in hydrocarboxylation of acetylene to acrylic acid using nickel catalyst, high conversion of acetylene was obtained only at above 5.0 MPa of CO [14]. If the pressure was lower, hydrocarboxylation reaction hardly occurred. This fully expressed that palladium catalyst has an excellent activity at low CO pressure, while nickel catalyst displays an excellent activity only at high CO pressure. In other words, low CO pressure favors formation of catalytic active species and in high pressure of CO, CO strongly coordinates toward Palladium center, hindering coordination of other substrates such as acetylene and alcohols. Many works have proved that CO has strong coordinating abilities for transition metals Pt, Ru, Pd [15, 35,36]. For example, in the structures of Pd-CO complexes line mode and bridge mode widely existed. In addition, when partial pressure of CO increased, acetylene occupation molar ratio in gas phase actually decreased; thus acetylene will be desorbed from solution. As is well known, the methoxycarbonylation of acetylene occurs in solution. Compared to entry 2, entry 3 in Table 4 proved to some degree that conversion of acetylene decreased since acetylene transferred from solution to gas phase at high total pressure of the system, resulting in decrease of acetylene concentration in solution. Similar results were obtained in our previous work [28]. Therefore, relative low pressure of CO was suitable for hydroesterification of acetylene with carbon monoxide to acrylates.

6. Effect of Reaction Temperature

Fig. 4 presents the effect of reaction temperature on the acetylene conversion for this reaction at about 27 °C, 50 °C and 75 °C, respectively. The conversion of acetylene enhanced drastically within 60 min when the reaction temperature was below 50 °C and changed a little with further increase of reaction time. However, the conversion of acetylene increased a little with an increase of reaction time at reaction temperature of 75 °C. It is noted that the conversion of

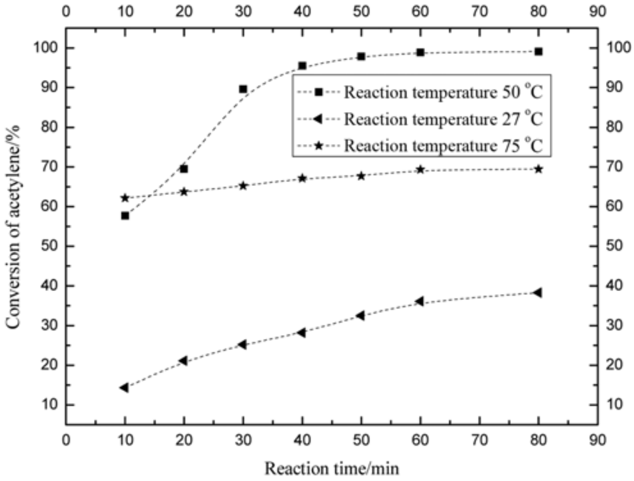


Fig. 4. Effect of reaction temperature with reaction time. Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, *p*-toluenesulfonic acid 1.1 mmol, acetone 50 ml, CH_3OH 12 ml, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa.

acetylene for 75 °C at 10 min of reaction time was above that for 50 °C, indicating that the initial reaction velocity was higher at higher temperature. It is a disadvantage for the catalyst at over-temperature such as 75 °C because a small amount of black palladium metal was observed at the bottom of reactor due to decomposition of the catalyst. But the reaction became very slow below 27 °C. Thus, we chose a reaction temperature of 50 °C to check the influence of other parameters on the reaction.

7. Effect of Alcohols

Table 6 shows the effect of aliphatic alcohols on the reaction. The conversion of acetylene decreased with an increase of carbon number in aliphatic alcohols. The highest acetylene conversion of 99.5% was achieved from methanol as a nucleophile, and the lowest acetylene conversion of 62.5% from n-dodecyl alcohol. This may be explained by the fact that with increase of carbon chain, nucleophilic attack was reduced because of steric hindrance. Although acetylene conversion was drastically affected with change of aliphatic alcohols, the selectivity toward n-esters remained above 99%.

Table 6. Effect of alcohols

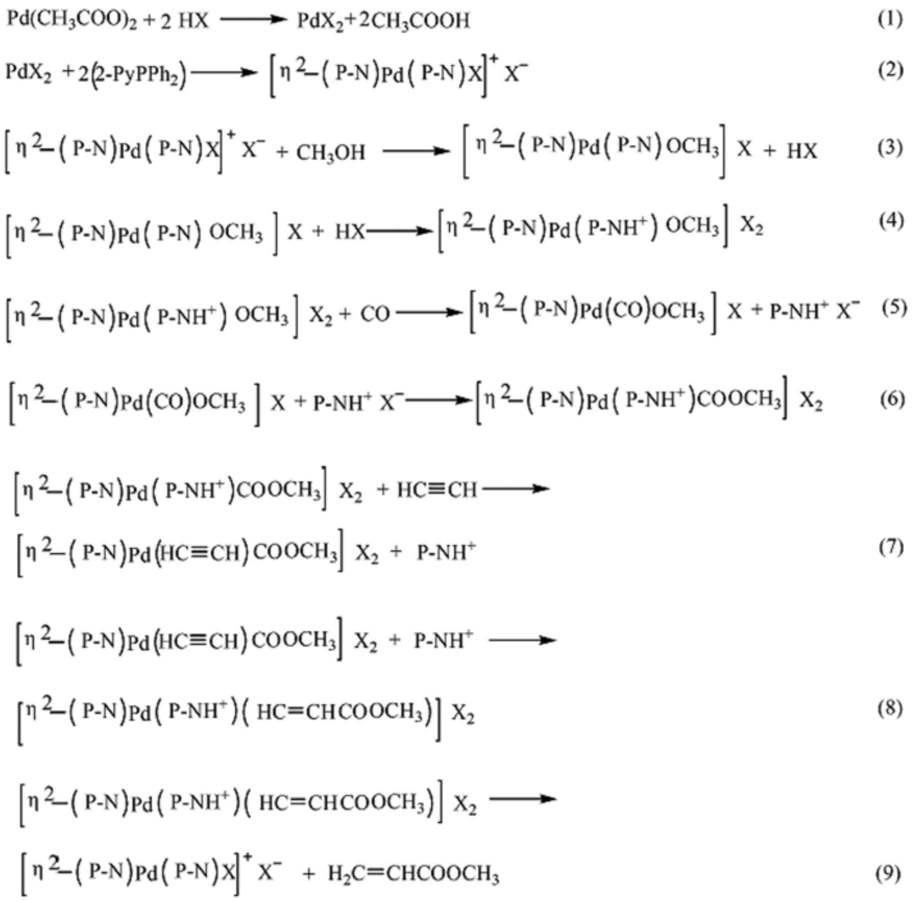
Alcohols	Conversion of acetylene/%	Selectivity/%	
		n-Ester	AA
Methanol	99.5	99.7	0.3
n-Propanol	72.6	99.6	0.4
n-Butanol	67.5	99.5	0.5
n-Hexyl alcohol	65.1	99.6	0.4
n-Dodecyl alcohol	62.5	99.5	0.5

Conditions: $Pd(OAc)_2$ 5.0×10^{-2} mmol, 2-$PyPPh_2$ 1.51 mmol, *p*-toluenesulfonic acid 1.1 mmol, acetone 50 ml, alcohol 0.3 mol, initial partial pressure: P(CO)=1.0 MPa, $P(C_2H_2)$=0.1 MPa, reaction temperature: 50 °C, reaction time: 60 min, AA: acrylic acid

It is noteworthy that the results obtained from our experiments are different from the results obtained by Bhattacharyya et al., which are higher acetylene conversion for longer carbon aliphatic alcohols [9-11]. The possible reasons lie in two ways. On one hand, the catalysts are different. Palladium catalyst combined with 2-$PyPPh_2$ ligand was used in this work, and in their work, nickel catalyst was used. On the other hand, reaction conditions are also different. The former was carried out at mild reaction conditions (50 °C, 1.0 MPa) and the latter at sloshing conditions (170 °C, 3.6 MPa). The difference may be ascribed to boil point of alcohols because the high temperature and the high pressure are beneficial for high boil point alcohols. Besides, the difference may be also relative to the catalysts because the catalytic activity of the former is higher than that of the latter. These results show that carbonylation reaction of acetylene is very sensitive to catalysts.

8. Reaction Mechanism

Based on our experiments, the following mechanisms, which



Scheme 2. Reaction mechanism. In reaction mechanism, HX symbolizes organic or inorganic acids, and P-N symbolizes the 2-$PyPPh_2$ ligand.

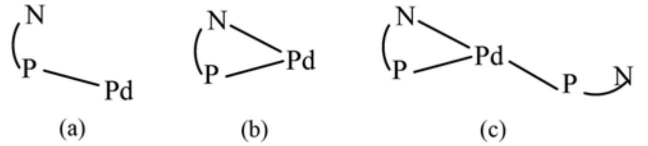


Fig. 5. Structures of palladium phosphorus complex.

are similar to the possible mechanisms presented to explain nickel or palladium catalyzed hydrocarboxylation of unsaturated hydrocarbons and palladium catalyzed hydroesterification of methylacetylene [3,7,13,26,30], may be proposed in Scheme 2:

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$_2$ towards palladium metal center to formation of $[\eta^2$-(P-N)Pd(P-N)X$]^+X^-$; thus the catalytic active species is formed. The cycle of catalytic reactions is composed of reactions (2)-(9).

PPh$_3$ was found to act as an excellent ligand for carbonylation reaction of unsaturated hydrocarbons such as styrene, phenylacetylene using palladium catalyst [5,30]. But it has no catalytic activity for methoxycarbonylation of acetylene as shown in Table 1, entries 8-12. Similarly, PPh$_3$ was also observed with lower activity in the methoxycarbonylation of propyne with carbon monoxide to methyl methacrylate [26]. 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$_2$. The active species is formed by reaction (2). However, PPh$_3$ coordinated toward palladium center, only forming monodentate complex with no activity or lower activity. There are three structures about palladium complex in the presence of 2-PyPPh$_2$ as given in Fig. 5.

The structure (a) is largely generated in high 2-PyPPh$_2$ concentration, and the structure (b) is largely formed in lower 2-PyPPh$_2$ concentration. The above two structures have no activity in the reaction. Therefore, the catalyst has lower activity when 2-PyPPh$_2$ is in high or lower concentration. The structure (c) with an excellent activity is mainly formed in the appropriate concentration of 2-PyPPh$_2$. To obtain high catalytic performance, the concentration of 2-PyPPh$_2$ should be appropriate in the reaction system.

In all acidic promoters, *p*-toluenesulfonic acid displayed an excellent activity. Trifluoromethane sulfonic acid is the strongest acid, but it has lower catalytic activity, suggesting that it is not beneficial to the reaction in the case of highest acidic strength. Besides, hydrochloric acid has a lower activity due to strong coordination of Cl^{-1} toward palladium center, causing decrease of displacement for other reaction molecules. Therefore, the acids with middle acidic strength and weak coordination of acidic anion play a key role in keeping an excellent catalytic performance.

To a certain extent, based on our experiments, the reaction mechanism has been elucidated. To fully understand the reaction mechanism about palladium catalyzed carbonylation of acetylene under such mild conditions, we will use some in situ techniques to investigate it in next work.

CONCLUSIONS

Methoxycarbonylation of acetylene has been carried out using a catalyst system containing Pd(OAc)$_2$, phosphorus ligands and acids under the CO initial partial pressures of 0.8-3.0 MPa at the temperatures of 27-75 °C. The catalytic activity was found strongly influenced by acidic promoters, and phosphine ligands. Furthermore N-P bidentate ligands play a crucial role for catalytic activity in this reaction. Other parameters such as alcohols, solvents, reaction time, reaction temperature and initial partial pressure of CO have also a great influence on the catalytic activity. Under the optimal experimental conditions, the catalyst system displayed an excellent catalytic performance with 99.5% of acetylene conversion, 99.7% of selectivity toward methyl acrylate and 2,502 h^{-1} TOF.

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SYMBOLS USED

n_0 : amount of fed acetylene [mol]
n_1 : amount of acetylene residue [mol]
n_P : amount of acetylene converted to product [mol]

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