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The Nickel and Copper-Catalyzed Hydroformylation of Acetylene with Carbon Monoxide to Acrylic Acid

**Congming Tang · Yi Zeng · Ping Cao ·
Xiangui Yang · Gongying Wang**

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Abstract A non-petroleum approach for the catalytic synthesis of acrylic acid by hydroformylation of acetylene with carbon monoxide has been studied under various conditions. Mixtures of nickel acetate tetrahydrate, cupric bromid, triphenylphosphine and methanesulfonic acid are used as catalysts, and tetrahydrofuran as solvent. The effect of cupric bromid, triphenylphosphine and methanesulfonic acid and water on the conversion of acetylene as well as the selectivity to acrylic acid has been studied. Triphenylphosphine is found to be effient for enhancement of the selectivity under the experimental conditions. When the reaction was carried out under the total initial pressure of 6.0 MPa at the temperature of 200 °C with the catalyst composition of 2.0 mmol $Ni(OAc)_2\,4H_2O$, 0.9 mmol $CuBr_2$, 2.0 mmol CH_3SO_3H and 4.0 mmol PPh_3, 90% conversion of acetylene and 90% selectivity to acrylic acid were achieved.

Keywords Non-petroleum synthesis · Acrylic acid · Nickel acetate tetrahydrate · Cupric bromid · Triphenylphosphine · Methanesulfonic acid

1 Introduction

Carbonylation of alkynes is one of the promising synthetic routes for unsaturated carboxylic acids/esters, having wide ranging applications as monomers for polymer synthesis, fine chemicals and pharmaceutical intermediates, etc. [1]. Carbonylation of acetylene with carbon monoxide to acrylic acid is viewed as a potential route for the direct synthesis of acrylic acid in the future because the other route for synthesis of acrylic acid through the partial oxidation of propene is facing the lack of petroleum, leading to the gradual increase of its cost [2]. The route for synthesis of acrylic acid through carbonylation of acetylene was firstly found by Reppe and his coworkers in 1939 [3]. They used $Ni(CO)_4$ as catalyst to catalyze acetylene, CO and water to acrylic acid. Since $Ni(CO)_4$ is highly poisonous, its commercial application as a catalyst must be limited and displaced by other catalysts [4, 5]. An exhaustive and intensive study on syntheses of acrylic acid through carbonylation of acetylene was made by Bhattacharyya S. K. and coworkers [6–8], using salts of iron, cobalt, and nickel as catalysts. 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 Jiaming Qiu [9]. The catalysts were demonstrated to catalyze the

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C. Tang · Y. Zeng · P. Cao · X. Yang · G. Wang
Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, 610041 Chengdu, Sichuan,
People's Republic of China
e-mail: tcmtang2001@163.com

C. Tang · G. Wang (✉)
College of Chemistry and Chemical Engineering, China West Normal University, 637002 Nanchong, Sichuan, People's Republic of China
e-mail: gywang@cioc.ac.cn

C. Tang · P. Cao
Changzhou Institute of Chemistry, 213164 Changzhou,
Jiangshu, People's Republic of China

C. Tang · P. Cao
Graduate School of Chinese Academy of Sciences,
10049 Beijing, People's Republic of China

carbonylation of acetylene under high CO pressure at high temperature with high conversion. But the major problems lie in carbon deposition, metal deposition and corrosion during the course of reaction.

The aim of this work was to develop an improved catalyst system for the carbonylation of acetylene, which can resolve the above problems to a certain extent, and give a higher conversion and a higher selectivity for the synthesis of acrylic acid.

2 Experimental

2.1 Materials

Nickel acetate tetrahydrate, cupric bromid, triphenylphosphine, methanesulfonic acid, *p*-toluene-sulfonic acid monohydrate, acrylic acid, acetylic acid, HCl, H_2SO_4, acetylene and carbon monoxide (all belonging to analytic grade) were used for the hydroformylation reaction without further purification.

2.2 General Procedure

Both liquid samples and gas samples were analysed on a SC-2000 Series GC, which is controlled by the N2000 Chemstation software, by using an packed column (2.6 m × 2 mm, on a poly(ethyleneglycol) 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, nickel acetate tetrahydrate (2.0 mmol), cupric bromid (0.9 mmol), triphenylphosphine (4.0 mmol) and methanesulfonic acid (2.0 mmol) were dissolved in a mixture of 97 mL tetrahydrofuran and 14 mL water and charged to the reactor. The reactor was firstly purged several times with nitrogen and subsequently pressurized with acetylene and to 0.5 MPa, and to 6.0 MPa with CO at room temperature. The reactants were heated up to 200 °C within 30 min. The reaction proceeded at 200 °C for 1 h, then the reaction system was cooled to room temperature. The gas samples and the liquid samples were immediately analyzed by gas chromatography.

Conversion of acetylene and selectivity to acrylic acid 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, amount of acetylene for input before reaction, n_1, amount of acetylene for residue after reaction, n_p, amount of acetylene for formation of acrylic acid.

3 Results and Discussion

3.1 Effect of PPh_3/Ni Ratio

The molar ratio of PPh_3 to Ni is found to have a significant role in product selectivity (Fig. 1). The selectivity to acrylic acid is very low, only 21% without phosphorous ligand of PPh_3. A marked increase in the selectivity is observed with increase in PPh_3/Ni ratio from 0 to 2.0. With a PPh_3/Ni ratio up to 2.0, the highest selectivity of 90% is achieved in the present conditions and the selectivity decreases with further increase in PPh_3/Ni ratio. But the selectivity changes a little when the ratio of PPh_3/Ni is above three. High selectivity can be mainly ascribed to PPh_3 for activating the CO molecule in presence of PPh_3 under the experimental conditions. With a PPh_3/Ni ratio of less one, substantial precipitation of the active catalyst to Ni metal is observed and no metal precipitation is observed above a ratio of 1.5. Because Ni metal has no catalytic activity for synthesis of acrylic acid, the selectivity is very low. In addition, the reactant of acetylene will be easily polymerized to produce by-products or hydrolyze to acetaldehyde under high pressure at high temperature if hydroformylation reaction does not occur. Metal precipitation and polymers of acetylene are very harmful for pipe, tubular reactor and other equipments in the application of industry.

A little decrease in the catalytic activity is observed with increase in PPh_3/Ni ratio. With increase in the concentration of PPh_3, it is likely that PPh_3 competes with the reactant molecules such as CO, acetylene for coordination toward Ni centre, causing decrease in the activity.

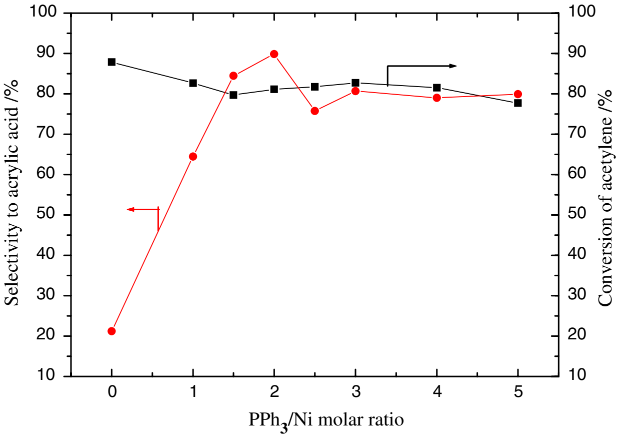

Fig. 1 Effect of PPh_3/Ni molar ratio on the carbonylation of acetylene. Conditions: $Ni(OAc)_2$ $4H_2O$ 2.0 mmol, $CuBr_2$ 0.9 mmol, CH_3SO_2OH 2.0 mmol, THF 98 mL, H_2O 12 mL, initial partial pressure: P(CO) = 5.7 MPa, P(C_2H_2) = 0.3 MPa

3.2 Effect of Cupric Bromid

Figure 2 suggests that the conversion of acetylene increases slightly with an increase in concentration of Cu^{2+}. When the molar ratio of Cu^{2+}/Ni^{2+} is above 0.6, the conversion of acetylene changes a little. The selectivity to acrylic acid is strongly affected by the concentration of Cu^{2+}. No acrylic acid is obtained without cupric bromid. Addition of a small amount of cupric bromid favors the formation of acrylic acid, and the selectivity to acrylic acid is higher, suggesting that copper is one of the main catalysts for the carbonylation of acetylene with carbon monoxide. The selectivity rapidly increases with an increase in concentration of cupric bromid and decreases drastically with further increase. When the molar ratio of Cu^{2+}/Ni^{2+} is 0.4, the selectivity of 85% is obtained. In the absence of copper(II), solubility of carbon monoxide is very poor in the mixture composed of tetrahydrofuran and water, so that the reaction of carbonylation of acetylene to acrylic acid hardly occurs. Thus copper(II) enhances the solubility of CO and activates CO molecule. However, the excess copper(II) will result in side reactions such as polymerization of acetylene and carbon deposition.

3.3 Effect of Different Acidic Promoters

The effect of different acidic promoters is given in Table 1. The activity decreases in the order methanesulfonic acid, *p*-toluenesulfonic acid, clorhydric acid, acrylic acid, acetylic acid, sulfuric acid, which accords with the order of acid strength of these acids with the exception of sulfuric acid. Higher activity and higher selectivity to product acrylic acid are observed with sulfonic acids in the present conditions. However the highest conversion (89.91%) and the highest selectivity (90.39%) are obtained in the case of methanesulfonic acid. The lowest conversion (44.50%) is obtained in the presence of sulfuric acid due to the formation of nickel sulfuric with having a low solubility.

Table 1 Effect of different acidic promoters

Acidic promoters	Conversion of acetylene/%	Selectivity to acrylic acid/%
Methanesulfonic acid	89.91	90.39
p-toluenesulfonic acid	84.06	79.05
Clorhydric acid	79.50	77.55
Acrylic acid	65.36	73.88
Acetylic acid	63.01	75.06
Sulfuric acid	44.50	75.45

Conditions: $Ni(OAc)_2\ 4H_2O$ 2.0 mmol, PPh_3 4.0 mmol, $CuBr_2$ 0.9 mmol, THF 97 mL, H_2O 14 mL, initial partial pressure: $P(CO)=5.5$ MPa, $P(C_2H_2) = 0.5$ MPa, reaction time: 40 min

3.4 Effect of Methanesulfonic Acid Concentration

The effect of the concentration of methanesulfonic acid is shown in Fig. 3. The catalytic activity decreases with increase of methanesulfonic acid and changes a little with further increase of methanesulfonic acid. The selectivity to acrylic acid is strongly affected by the methanesulfonic acid. The selectivity is lower without methanesulfonic acid and increases drastically with increase in methanesulfonic acid concentration, and the highest selectivity of about 85% is observed as the ratio of CH_3SO_3H/Ni is increased to one. But the selectivity decreases drastically when the ratio

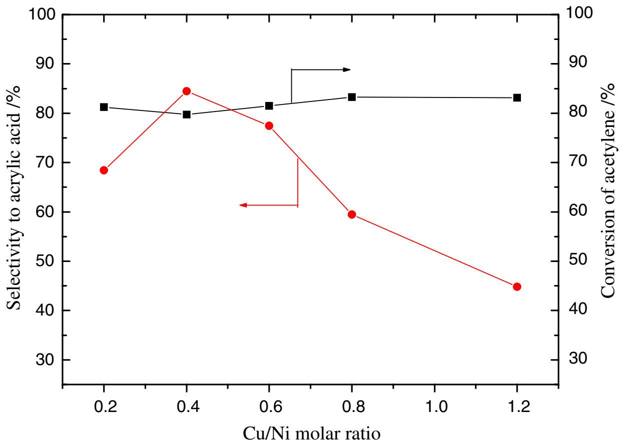

Fig. 2 Effect of Cu/Ni molar ratio in the carbonylation of acetylene. Conditions: $Ni(OAc)_2\ 4H_2O$ 2.0 mmol, PPh_3 4.0 mmol, CH_3SO_2OH 2.0 mmol, THF 98 mL, H_2O 12 mL, initial partial pressure: $P(CO) = 5.7$ MPa, $P(C_2H_2) = 0.3$ MPa

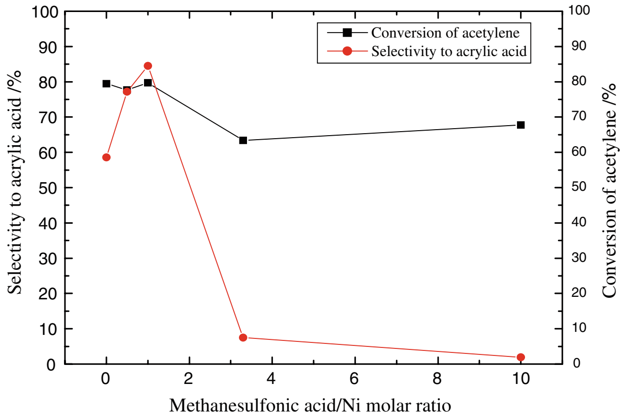

Fig. 3 Effect of methanesulfonic acid concentration. Conditions: $Ni(OAc)_2\ 4H_2O$ 2.0 mmol, $CuBr_2$ 0.9 mmol, PPh_3 4.0 mmol, THF 98 mL, H_2O 12 mL, initial partial pressure:$P(CO) = 5.7$ MPa, $P(C_2H_2) = 0.3$ MPa

Table 2 Effect of H_2O on the carbonylation of acetylene

$V(H_2O)$: $V(THF)$	Conversion of acetylene/%	Selectivity to acrylic acid/%
12:97	89.85	83.73
14:97	83.91	80.59
15:97	84.92	79.41
16:97	83.24	80.15
18:97	83.12	72.97
20:97	84.20	70.73

Conditions: $Ni(OAc)_2\ 4H_2O$ 2.0 mmol, $CuBr_2$ 0.9 mmol, PPh_3 4.0 mmol, CH_3SO_2OH 2.0 mmol, THF 97 mL, initial partial pressure: $P(CO) = 5.5$ MPa, $P(C_2H_2) = 0.5$ MPa

is above one. For example, the selectivity is less than 10% when the ratio is above three. The possible reason is that in an appropriate amount of CH_3SO_3H, the formation of $HNi(PPh_3)_2X$ is easier than that without CH_3SO_3H, so the selectivity enhances greatly. But in excess of CH_3SO_3H, the ability of CO for displacement of $CH_3SO_3^-$ decreases due to the competition of $CH_3SO_3^-$ with CO for coordination toward the centre of Ni, causing decrease in the ability of activation for CO, thus the selectivity decreases drastically.

3.5 Effect of H_2O

The effect of H_2O on the carbonylation of acetylene with carbon monoxide to acrylic acid is shown in Table 2. The conversion of acetylene changes a little with an increase of H_2O, but the selectivity to acrylic acid changes greatly with an increase of H_2O. In the scope of 12–16 mL of H_2O, the selectivity changes a little, and decreases sharply with further increase of H_2O up to 18 mL. It is likely that the polarity of solution is enhanced due to solvent effect, leading to a decrease in solubility of CO and C_2H_2 in the solution. Thus this causes the decrease in the selectivity. The solubility of acetylene is shown in Fig. 4. The solubility of acetylene decrease gradually with increase of H_2O in the $THF–H_2O$ system under the experimental conditions.

3.6 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 [4, 10–12], may be proposed:

$$Ni(CH_3COO)_2 + 2HX \rightarrow NiX_2 + 2CH_3COOH \quad (1)$$

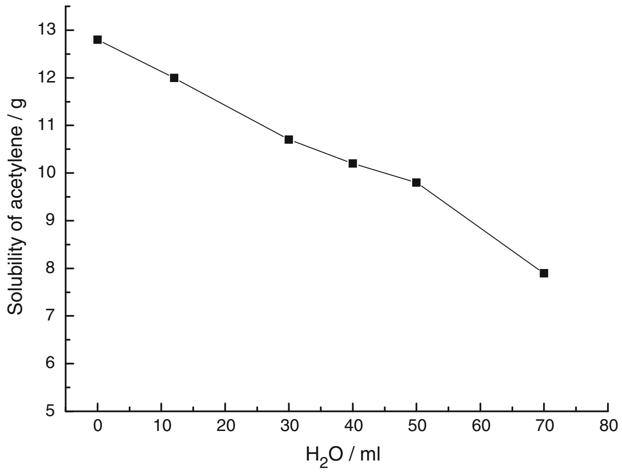

Fig. 4 Solubility of acetylene in the $THF–H_2O$ system. Conditions: $Ni(OAc)_2\ 4H_2O$ 2.0 mmol, $CuBr_2$ 0.9 mmol, PPh_3 4.0 mmol, THF 97 mL, CH_3SO_2OH 2.0 mmol, $P(C_2H_2) = 0.5$ MPa

$$NiX_2 + 2PPh_3 \rightarrow (Ph_3P)_2NiX_2 \quad (2)$$

$$(Ph_3P)_2NiX_2 + H_2O \rightarrow HNi(PPh_3)_2X + HX \quad (3)$$

$$HNi(PPh_3)_2X + CO \rightarrow HNi(PPh_3)_2CO + X^- \quad (4)$$

$$HNi(PPh_3)_2CO + HC{\equiv}CH \rightarrow (HC{\equiv}CH)HNi(PPh_3)_2CO \quad (5)$$

$$(HC{\equiv}CH)HNi(PPh_3)_2CO \rightarrow H_2C{=}CH{-}Ni(PPh_3)_2CO \quad (6)$$

$$H_2C{=}CH{-}Ni(PPh_3)_2CO \rightarrow H_2C{=}CHCONi(PPh_3)_2 \quad (7)$$

$$H_2C{=}CHCONi(PPh_3)_2 + X^- \rightarrow H_2C{=}CHCONi(PPh_3)_2X \quad (8)$$

$$H_2C{=}CHCONi(PPh_3)_2X + H_2O \rightarrow HNi(PPh_3)_2X + H_2C{=}CHCOOH \quad (9)$$

where, HX = organic or inorganic acids.

Reaction (1) is that anions X of strong acids (HX) displace the acetate anion from nickel acetate via a simple acid–base reaction, thus generating cationic nickel(II) species. Reaction (2) is coordination of PPh_3 towards nickel metal centre, which plays an important role in the stabilization of catalytic nickel(II). Reaction (3) is the formation of catalyst, which is the key step to synthesize acrylic acid selectively. Those reactions are supported by the experimental finding that the selectivity to acrylic acid markedly increased with the rise of concentration of PPh_3. The cycle of catalytic reactions is composed of reaction (3–9).

PPh_3 with a good σ-donor and a poor π-acceptor can increase the electron density of nickel centre. This favors the stability of Ni–H and the coordination of CO towards

Ni centre so that the selectivity to acrylic acid is enhanced drastically. In the absence of PPh_3, Ni(II) is easily reduced and can not easily activate the molecule of CO, so the selectivity is very low. While in excess of PPh_3 in the reaction system, the selectivity decreases a little, ascribing to the competition of PPh_3 with reactants such as CO, C_2H_2. As for anions X^-, if they have poorer ability of coordination towards Ni centre, CO can easily displace them, which favors the reaction and the selectivity to acrylic acid. It is very interesting that the highest selectivity is obtained as the ratio of $X^-(CH_3SO_3^-)$/Ni and the ratio of PPh_3/Ni is one and two, respectively, and the ratios coincide with the structure of active species of $HNi(PPh_3)_2X$.

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

4 Conclusions

Ni catalyst with copper and methanesulfonic acid promoters is an efficient catalyst for the direct synthesis of acrylic acid by the hydroformylation of acetylene with carbon monoxide. The high selectivity to acrylic acid (90%) and the high conversion of acetylene (90%) could be obtained under the optimal experimental conditions. Neither metal precipitation nor polymers of acetylene is found in the reaction system. Such results indicate that it will be obtained a potential application in the production of chemical industry.

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