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Effects of Alkali Halide Salts on Hydrocarboxylation of Styrene Catalyzed by Water-Soluble Palladium Phosphine Complexes

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Abstract Hydrocarboxylation of styrene catalyzed by water-soluble Pd-TPPTS complexes was investigated. The reaction conditions, including reaction pressure, temperature, time and etc. have a significant influence on the catalytic performance. It was found that the yield of total acids and the selectivity towards 3-phenylpropionic acid were enhanced by adding a suitable amount of alkali metal halide salts. In addition, the reaction mechanism and the role of alkali metal halide salts in the reaction were discussed on the basis of the characterization of ^{1}H NMR and ^{31}P NMR.

Keywords Aqueous two-phase system · Hydrocarboxylation · Palladium-phosphine complexes · Alkali metal halide

1 Introduction

Hydrocarboxylation of olefins as one of the important methods for the functionalization of olefinic double bond, is a very promising and environmentally friendly method for obtaining carboxylic acids [1]. Palladium-catalyzed hydrocarboxylation, i.e. olefins, CO and water catalyzed by palladium to produce acid has been quite extensively studied in the past several decades, especially in the synthesis of 2-phenylpropionic acids and its derivatives, which are applied as potential precursors in non-steroidal anti-inflammatory drugs such as naproxen and ibuprofen [2, 3], while the linear products of hydrocarboxylation of vinyl aromatics such as 3-phenylpropionic acid, have also been found application as special chemicals [4, 5] (Scheme 1).

Aqueous/organic biphasic catalysis has received widespread attention due to the advantages of environmentally benign process and the readily efficient separation of the catalyst from the products [6, 7]. Water acts not only as one of the reactant, but as the solvent in hydrocarboxylation. Water-soluble phosphine ligands are always used to coordinate with noble metal catalyst in order to separate from organic products and to recover the noble metal catalyst. In this aspect, water-soluble phosphine ligands TPPTS (trisulfonated triphenylphosphine), TPPMS (monosulfonated triphenyl-phosphane) [8–10], and amphiphilic ligand like *N*-bis(*N*',*N*'-diethyl-2-aminoethyl)-4-aminomethylpheneyl-dephenylphosphine (N3P) [11] have been employed in the palladium-catalyzed aqueous hydrocarboxylation reaction. Among these ligands, TPPTS as a highly water-soluble ligand has attracted great attention due to its good solubility and excellent characteristics of coordination to palladium and so far, the only one with an industrial application in biphasic processes [12–14].

The study of promoters has been a common theme in the development of aqueous two-phase catalytic system [15]. In the hydrocarboxylation, two essential additives have been used. The first one is Brønsted acid (H^{+}), which plays a very important role in the hydrocarboxylation since it can

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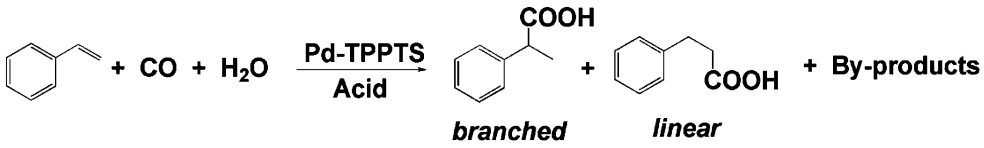
Scheme 1 The hydrocarboxylation of styrene



promote to form the species like $[HPd(CO)L_3]^+$ (L=phosphine ligand), which is one of the catalytically active species. There is almost no product of carboxylic acid if Brønsted acid is absent. The cationic surfactants including cetyltrimethylammonium bromide (CTAB), hexadecyltrimethylammonium chloride (CTAC) etc., and especially chemically modified β-cyclodextrins have been used to solve the mass transfer limitation in the case of hydrocarboxylation of the long-chain olefins [16, 17]. However, except the two promoters employed above, the metal salts have been examined as the third promoter to improve the activity or selectivity. For instance, Yuan et al. [18] has found that addition of basic alkali metal salts (Na_2CO_3, K_2CO_3, and NaH_2PO_4) could promote the hydroformylation performance with supported aqueous-phase catalysts (SAPC) (fumed-SiO_2-SAPC) by inhibiting the oxidation of ligand TPPTS to trisulfonated triphenylphosphine oxide (OTPPTS). In addition, alkali metal chloride is also used as a promoter in the carbonylation reaction [19]. LiCl has been used as a promoter to catalyze the hydrocarboxylation of alkenes or alcohols to acids with the Pd complex [Pd(pyca)(PPh_3)(OTs)] which was anchored in highly ordered mesoporous silica such as Pd-pyca-MCM-41 or Pd-pyca-MCM-48 materials [20]. Aghmiz [14] has indicated that the presence of Cl^- anion (from adding NaCl) in the aqueous phase can increase the stability of the catalytic system.

Although different metal halide salts have been employed to promote the hydrocarboxylation of styrene up to now, the detailed mechanism why the salts have an influence on the reaction still remain not very clear. On the basis of the previous research above, in this work, we investigate the effects of different alkali metal halide salts on the yield of acids, selectivity of products, and catalytic stability for the hydrocarboxylation of styrene by using Pd-TPPTS catalytic system. Meanwhile, the spectra of ^{1}H NMR and ^{31}P NMR were utilized to investigate the interaction between alkali halide and Pd-TPPTS complexes and attempted to gain a deeper insight into the mechanism of hydrocarboxylation of olefins.

2 Experimental

2.1 Materials and Methods

$Pd(OAc)_2$ was received by Sinopharm Chemical Reagent Co.Ltd, TPPTS was purchased from Jintan Gaode Chemical Co., Ltd, China and recrystallized before uses. CO with a purity of >99.95 % was provided by Beijing Longhui Jingcheng Gas Co., Ltd. Styrene was received by Shanhai Shanpu Chemical Co., Ltd. Sodium *p*-styrenesulfonate was provided by J&K Chemical. All solvents used were distilled and deoxygenated prior to use. All other reagents were commercial samples and were used as purchased.

Gas chromatography analyses were performed on a gas chromatograph (SP-2100, Beijing Beifen-Ruili Analytical Instrument, China) equipped with an FID detector and a capillary column (50 m × 0.25 mm) HP-5, and N_2 was the carrier gas. FT-IR spectra were measured by a Nicolet 6700 FT-IR spectrometer. GC–MS analyses were detected by Turbomass-Autosystem XL (PerkinElmer Inc., USA).

All NMR experiments were carried out with standard Schlenk techniques. The NMR spectrums were recorded on a Varian VNMRS 600 spectrometer with an observation frequency of 242.9 MHz for ^{31}P NMR in D_2O solution with respect to 85 % H_3PO_4 (at room temperature), and of 600 MHz for ^{1}H NMR. In the ^{1}H NMR measurements, D_2O, sodium *p*-styrenesulfonate, $Pd(OAc)_2$, TPPTS, and *p*-TsOH were added into the autoclave successively. Carbon monoxide was charged up to desired pressure after removing the air by pressurizing-depressurizing cycles with CO for five times. When the autoclave was heated to desired temperature, the stirring held for another 2 h. After the reaction completed, the autoclave was cooled and slightly yellow D_2O solution was removed from autoclave for NMR measurement. All ^{1}H NMR spectra were measured under 0.1 MPa N_2 atmospheres at room temperature. In the ^{31}P NMR measurement, $Pd(OAc)_2$, TPPTS, *p*-TsOH, alkali halide salts and CO were added to the autoclave successively. The procedures were the same as that for ^{1}H NMR measurement except that all ^{31}P NMR was measured under 0.1 MPa CO atmospheres.

2.2 Standard procedure for hydrocarboxylation reaction

All reactions and manipulations were carried out in a 100 ml stainless steel which was placed in an oil bath with a magnetic stirrer. The mixture was placed in a glass vessel containing a stirring bar to protect the acid solution from direct contact with the wall of stainless steel.

The catalysts of palladium-phosphine complexes were in situ prepared during the reaction. A typical procedure of aqueous-organic biphasic hydrocarboxylation reaction of styrene was conducted as follows: catalyst precursor

$Pd(OAc)_2$, TPPTS, acid and a certain amount of alkali metal salts were added into the glass vessel and dissolved in deoxygenated distilled water. The organic layer was a mixture of styrene, 2,6-di-tert-butylphenol (as inhibitors) and undecane (as an internal standard for gas chromatograph analysis) were charged into the previous solution in the glass vessel. The autoclave was sealed after the glass vessel was moved in. After five pressurizing-depressurizing cycles with CO to remove the air, the autoclave was pressurized to desired value and then placed in a silicone oil-bath. The solution was stirred for 30 min at ambient temperature to dissolve all of the solids. The reaction mixture was maintained for a given time after the autoclave was heated to the desired temperature. After the reaction completed, the stirring was stopped and the autoclave was cooled quickly with ice water to ambient temperature. The autoclave was vented slowly to atmospheric pressure. The liquid was transferred to a separatory funnel and the aqueous phase was extracted with ethyl acetate three times (15 ml × 3). The yield and *l/b* molar ratio of the acid products was detected by GC after they were esterified into methyl esters.

3 Results and Discussions

3.1 Hydrocarboxylation of Styrene with Pd-TPPTS Complexes

In the hydrocarboxylation of styrene, two major products were generated, i.e., 2-phenylpropionic acid (2-**PPA**, branched) and 3-phenylpropionic acid (3-**PPA**, linear). It has been known that the molar ratio of *l/b* could be affected by the reaction temperature, CO pressure and ligand et al. [21, 22]. In addition, the side reaction, e.g., polymerization of styrene was inevitable under the reaction conditions due to highly activated C=C double bonds of styrene, especially at the high temperature [23].

Firstly, the different reaction conditions were examined for hydrocarboxylation of styrene in the present work and the results were shown in Table 1. The yield of 3-**PPA** and 2-**PPA** were increased with the temperature continuously from 80 to 130 °C. The yield of 3-**PPA** and 2-**PPA** was only 21.5 and 23.7 % at 80 °C, but the yield of 3-**PPA** and 2-**PPA** up to 41.6 and 34.9 % when the reaction temperature was increased to 130 °C, respectively. However, the ratio of *l/b* almost remained unchanged as the temperature increased (Table 1, entry 1, 2 and 3). In addition, the yield of total acids (3-**PPA** and 2-**PPA**) only increased slightly and the molar ratio of *l/b* did not change considerably when the molar ratio of P/Pd decreased from 25 to 5 (Table 1, entry 3, 5 and 6). However, it was found that metallic palladium (palladium black) was precipitated when the molar ratio of P/Pd was lower than 5. The CO pressure can affect the reaction considerably, which indicated the yield of total acids was increase with the CO pressure increased from 2 MPa to 4 MPa (Table 1, entry 7, 8 and 3), but the higher pressure can not contribute to the yield of acid obviously (Table 1, entry 3 vs 9). Furthermore, when the reaction time increased from 5 to 7 h, the yield of 3-**PPA** and 2-**PPA** did not improve at all (Table 1, entry 3 and 4). Based on the catalytic results above, the optimized conditions as shown by entry 3 in table 1 have been used to the following investigation.

3.2 Effect of Alkali Metal Halide on the Catalytic Performance

Although metal halide promoters have been used in carbonylation, particularly in hydrocarboxylation [7, 19, 24], the detailed reason why the salts can promote the hydrocarboxylation reaction are still obscure. In order to understand the role of halide promoters played in the hydrocarboxylation of styrene, three kinds of alkali metal halide salts, i.e. alkali metal chlorides, alkali metal bromides and alkali metal iodides were screened under the same conditions and the results were discussed as follows.

To examine the roles of different halide anions in hydrocarboxylation, the effect of adding potassium chloride was firstly examined with the different molar ratio

Table 1 Reaction effect of several parameters on the hydrocarboxylation of styrene

Entry	T(°C)	P/Pd[a]	P_{CO} (MPa)	Yield (%)			*l/b*[e]
				3-**PPA**[b]	2-**PPA**[c]	By-products[d]	
1	80	25	4	21.5	23.7	15.5	0.91
2	110	25	4	36.9	32.4	19.0	1.05
3	130	25	4	41.6	34.9	19.0	1.09
4[f]	130	25	4	43.8	35.6	19.2	1.13
5	130	15	4	42.7	36.8	17.6	1.06
6[g]	130	5	4	36.3	44.8	16.4	0.81
7	130	25	2	9.7	7.5	16.3	1.30
8	130	25	3	25.2	22.1	29.1	1.19
9	130	25	5	42.0	37.5	16.3	1.06

Reaction conditions: *p*-TsOH (0.041 mol/L), H_2O (0.89 mol), styrene (9.62 mmol); reaction time: 5.0 h

[a] Molar ratio of TPPTS to Pd atoms

[b] 3-Phenylpropionic acid

[c] 2-Phenylpropionic acid

[d] The major by-product was polystyrene, and its structure was determined by ^{13}C NMR and FT-IR (see supporting information)

[e] Molar ratio of linear acid to branched acid

[f] Reaction time: 7 h

[g] Palladium black was observed after the reaction

KCl/Pd ranged from 1 to 32, and the results were presented in Fig. 1a. It can be seen that increasing molar ratio of KCl/Pd from 1 to 4 did not improve the yield of total acids obviously. On the contrary, when the molar ratio of KCl/Pd was more than four the yield of the total acids decreased considerably. However, as shown in Fig. 1b, the addition of KBr can indeed enhance the yield of the total acids obviously when the molar ratio of KBr/Pd was lower than four, but the more addition of KBr (the molar ratio of KBr/Pd > 8) resulted in the slight decrease in yield of total acids. The effects of potassium iodide on hydrocarboxylation were also studied and results were shown in Fig. 1c. Similar to that of KBr, it was beneficial to hydrocarboxylation of styrene when the molar ratio of KI/Pd was near two, but the yield of total acids dropped down rapidly if the molar ratio of KI/Pd was increased further.

It can be seen from Fig. 1a, b, c) that an appropriate amount of potassium halide was favorable to the hydrocarboxylation reaction, which can be attributed to the stabilization role of halide to Pd-TPPTS complex. Because the coordination ability of halide anions was increased in the order: $Cl^- < Br^- < I^-$, it was expected that chloride ions have weak coordination ability with Pd center and so cannot stabilize Pd(II)-TPPTS complex effectively. In contrast, iodide ion would possess highest nucleophilicity, implying iodide ion can coordinate strongly with Pd center. However, the strong coordination of iodide ion can result in blocking active center of central metal and inhibited the coordination and activation of styrene and CO on complex. The present results confirmed that bromide ions made a good compromise between coordination ability and stability of complex. It should be noticed that when an excess of halide ions was added, the yield of total acid was decreased in all cases, which resulted from that the ionic strength in aqueous phase was increased by adding more salts. The solubility of styrene in water was decreased accordingly as ionic strength increased and was expected to further decrease the yield of total acids [19, 25].

In the next step, we examined effects of alkali metal salts on the reaction by using the same halide anions. As shown in Fig. 2, MX/Pd (molar ratio) $= 2$ was employed in all cases. It can be observed that the addition of alkali metal bromides improved catalytic activity of the original Pd-TPPTS system considerably and afforded the higher yield of total acids than that of alkali metal iodides when the same cations were used. Although the addition of alkali metal chlorides (NaCl and KCl) did not improve the catalytic performance, the addition of LiCl was found to be the beneficial to the hydrocarboxylation of styrene as that of alkali metal bromides.

In summary, the addition of bromide anions gave the best result for the hydrocarboxylation of styrene among halide anions used. The different alkali metal cations seemed to have a small impact on the hydrocarboxylation reaction except LiCl. Interestingly, adding alkali metal halide salts led to the increase in the selectivity towards to 3-**PPA** in the order: MI > MBr > MCl, which was well consistent with that of halide nucleophilicity. This implied the strong coordination of halide anions with Pd center would favor the formation of linear product. Furthermore, the hydrocarboxylation of styrene was facilitated by adding appropriate amount of alkali metal halides due to the stabilization of Pd center by halide anions, but the reaction can be suppressed by adding excess amount of alkali metal

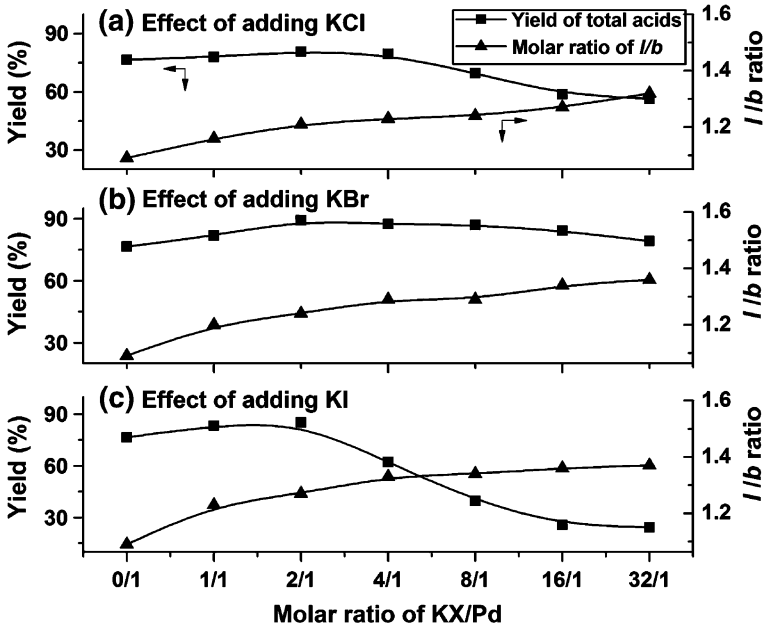


Fig. 1 The effect of adding KX on the hydrocarboxylation of styrene. X represents Cl^-, Br^- and I^-, respectively

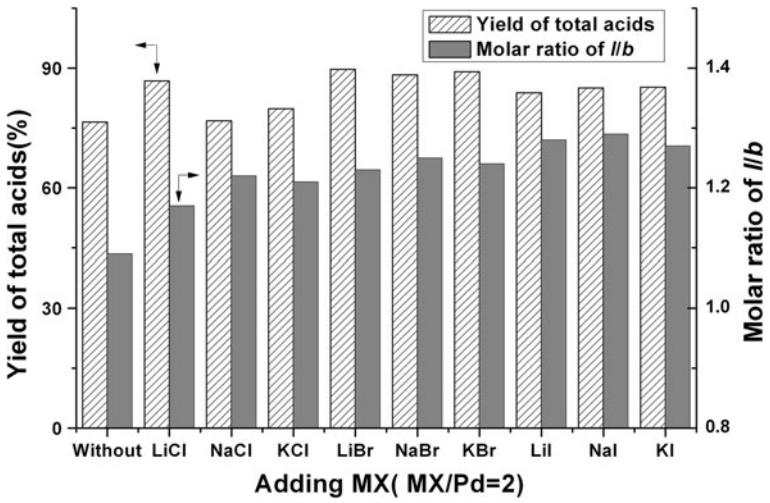


Fig. 2 Effect of the different alkali halide on the hydrocarboxylation of styrene (MX/Pd molar ratio = 2)

halides, because an excess of salt in water decreased the solubility of styrene in water, and also an excess of halide ions likely blocked the active center.

3.3 NMR characterization of catalytic aqueous phase modified by alkali metal halide

To illustrate the roles of adding alkali metal halide salts in hydrocarboxylation of styrene, the spectra of ^{31}P NMR of different catalytic aqueous solution were measured under 0.1 MPa of CO after reaction and the results were displayed as Fig. 3. The signals (δ) around 33.9–34.2 can be attributed to $[Pd(TPPTS)_3]X_2$ species (X = anions) [26, 27]. Particularly, 33.99 (t, J_{PP} = 126,132 Hz) resulted from the signals of $[Pd(TPPTS)_3]^{2+}(OTs^-)_2$ species (Fig. 3a); 34.01 (t, J_{PP} = 126,132 Hz) the signals of $[Pd(TPPTS)_3]^{2+}(Cl^-)_2$ (Fig. 3b); 34.07 (t, J_{PP} = 132,132 Hz) the signals of $[Pd(TPPTS)_3]^{2+}(Br^-)_2$ (Fig. 3c); and 34.13(t, J_{PP} = 126,138 Hz) the signals of $[Pd(TPPTS)_3]^{2+}(I^-)_2$ (Fig. 3d), respectively. Additionally, the signals at 22.4–22.7 were attributed to $HPd(0)(TPPTS)_3X$ (X= OTs^-, Cl^-, Br^-, I^-) [26, 28]. The signals at 36.17 were attributed to oxidized TPPTS (OTPPTS). The broad peaks at δ 1.0–2.2 were attributed to free TPPTS ligand exchanged with Pd-TPPTS complexes [27, 29].

From Fig. 3, It can be found that the amount of Pd(0) complex $[HPd(0)(TPPTS)_3]X$, which was considered as one of the catalytically active species decreased from (a) to (d) accordingly, which demonstrated that adding appropriate amount of KX (X= Cl^-, Br^-, I^-; the molar ratio of KX/Pd=2) would suppress the formation of Pd(0) species. In other words, Pd(II) species were stabilized by halide anions in the order: $I^- > Br^- > Cl^-$, implying that a highly nucleophilic anion can coordinate with Pd(II) center, and to inhibit the reduction of Pd(II) species [30].

Subsequently, to illustrate further the detailed mechanism by which alkali metal halide salts were added to promote the hydrocarboxylation of styrene, the spectra of ^1H NMR were measured in the course of hydrocarboxylation reaction. The sodium *p*-styrenesulfonate was used as a reactant in ^1H NMR measurement because the sodium *p*-styrenesulfonate was water-soluble and thus the homogeneous solution was suitable for NMR measurement. On the other hand, the single phase can overcome the mass transfer, and was favorable to hydrocarboxylation. The hydrocarboxylation reaction has been shown in Scheme 2, and the linear and branched products can be identified by ^1H NMR measurement by using D_2O as reaction media, respectively.

The spectra of ^1H NMR for a solution of sodium *p*-styrenesulfonate have been measured under 0.1 MPa N_2 atmosphere after reaction. As shown in Fig. 4a, b, the proton chemical shift arisen from sodium *p*-styrenesulfonate molecule have been labeled. It can be seen that the protons (H^1, H^2 and H^3) from sodium *p*-styrenesulfonate gave multi-peaks in D_2O, but when sodium *p*-styrenesulfonate was coordinated with Pd-TPPTS complex, the NMR signals (6.86, 5.98, 5.45), corresponding to (H^1, H^2 and H^3), was shifted to higher field (6.70, 5.83 and 5.32), and afforded a broad single peak, respectively (Fig. 4b). Furthermore, the proton chemical shift from phenyl group (H^5) almost disappeared from its original 7.6 due to the coordination of Pd-TPPTS with sodium *p*-styrenesulfonate. These results implied that the C=C bonds in sodium *p*-styrenesulfonate can coordinate and activated with Pd-TPPTS even at room temperature, and more possibly, phenyl group also have strong interaction with Pd center [31]. The possible structure of coordination has been given in Fig. 4.

The ^1H NMR spectra of sodium *p*-styrenesulfonate was also measured after reaction under 50 and 90 °C, and the

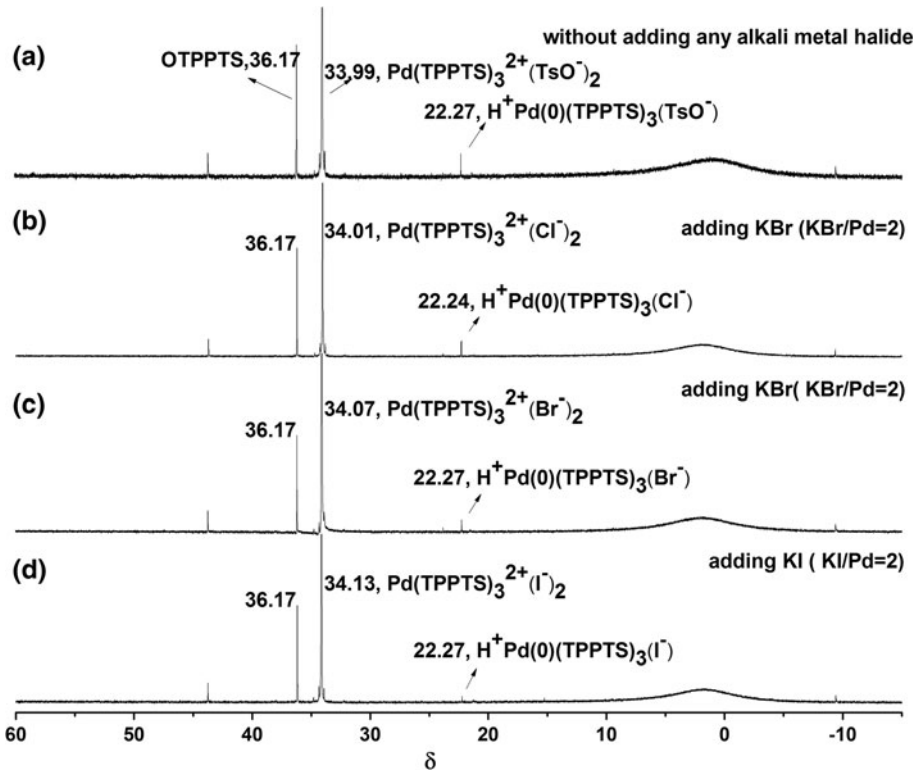
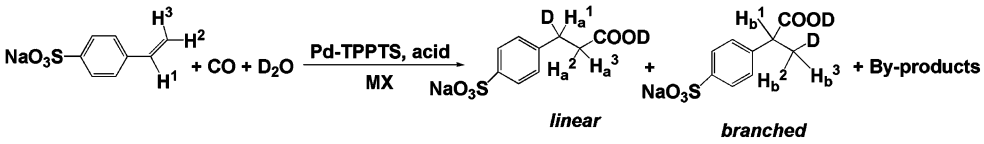


Fig. 3 ^{31}P NMR spectrums of Pd-TPPTS complex in D_2O solution under 0.1 MPa CO atmosphere: **a** $Pd(OAc)_2$, TPPTS, *p*-TsOH, CO; **b** KCl (molar ratio of KCl/Pd=2), $Pd(OAc)_2$, TPPTS, *p*-TsOH, CO; **c** KBr (molar ratio of KBr/Pd=2), $Pd(OAc)_2$, TPPTS, *p*-TsOH, CO; **d** KI (molar ratio of KI/Pd=2), $Pd(OAc)_2$, TPPTS, *p*-TsOH, CO. Reaction conditions: room temperature for 2 h, D_2O = 1.0 ml, $Pd(OAc)_2$ = 0.04 mmol, P/Pd = 8, *p*-TsOH = 0.2 mmol, and P_{CO} = 4 MPa



Scheme 2 The hydrocarboxylation of sodium *p*-styrenesulfonate

results were shown in Figs. 5 and 6, respectively. It can be observed that a very small amount of **3-PPA** and **2-PPA** were produced without alkali metal halide under 50 °C condition, but the amount of both acids increased considerably when KBr was added (KBr/Pd=2) (Fig. 5b). If the reaction temperature increased to 90 °C (Fig. 6a, b), the chemical shift (δ = 5–7) assigned to protons in C=C bond of sodium *p*-styrenesulfonate was completely disappeared without or with addition of KBr, and NMR signals resulted from **3-PPA** and **2-PPA** became stronger, as compared with that reacted at 50 °C. In addition, it can be found that the molar ratio of *l*/*b* (represented by the peak area of H_a^2, H_a^3/H_b^2, H_b^3) was 0.72 in the absence of any salt, while this ratio was increased up to 1.11 in the presence of KBr (KBr/Pd was 2) (Fig. 6), which was in good agreement with the results shown in Fig. 1.

3.4 The Proposed Mechanism for Hydrocarboxylation

Although the mechanism of hydrocarboxylation of olefins catalyzed by Pd-TPPTS complexes has been investigated in previous reports [32, 33], the roles of Pd center and salt additive in the reaction was controversial, and especially the oxido-reduction of Pd(II) to Pd(0) was not well defined in water [34]. Generally, two roles of Pd center in the popular mechanism have been proposed for hydrocarboxylation, i.e. the hydrido-Pd mechanism [5], the first involved Pd(0) species [21] and the second one the Pd(II) species [28, 30, 35], respectively. According to the present catalytic system, the presence of halide salt can stabilize Pd(II)-TPPTS species and thus favored the formation of the linear acids. Based on discussion above, the results can be explained by the mechanism illustrated in Scheme 3. In the cycle **1** involving in Pd(0) species, the $[Pd(II)TPPTS]^{2+}$ was first reduced to $[HPd(0)(TPPTS)^3]^+$ by CO and TPPTS, and then the coordinated styrene inserted into a Pd-H bond to form metal-alkyl species. With further, CO migrated and inserted into an alkyl-metal bond to form an acyl-metal complex, which was attacked nucleophilically by H_2O to produce the linear or branched acid. Meanwhile, the Pd hydride complex was regenerated. In the cycle **2**, a Pd(II) complex $[HPd(X)(CO)(TPPTS)]^{2+}$ was inserted by olefin to form an alkyl-metal complex with a linear preference. An acyl-metal bond was formed by the migratory insertion of CO. The linear product was mainly formed and the catalyst cycle was completed after water attacked the acyl-metal complex.

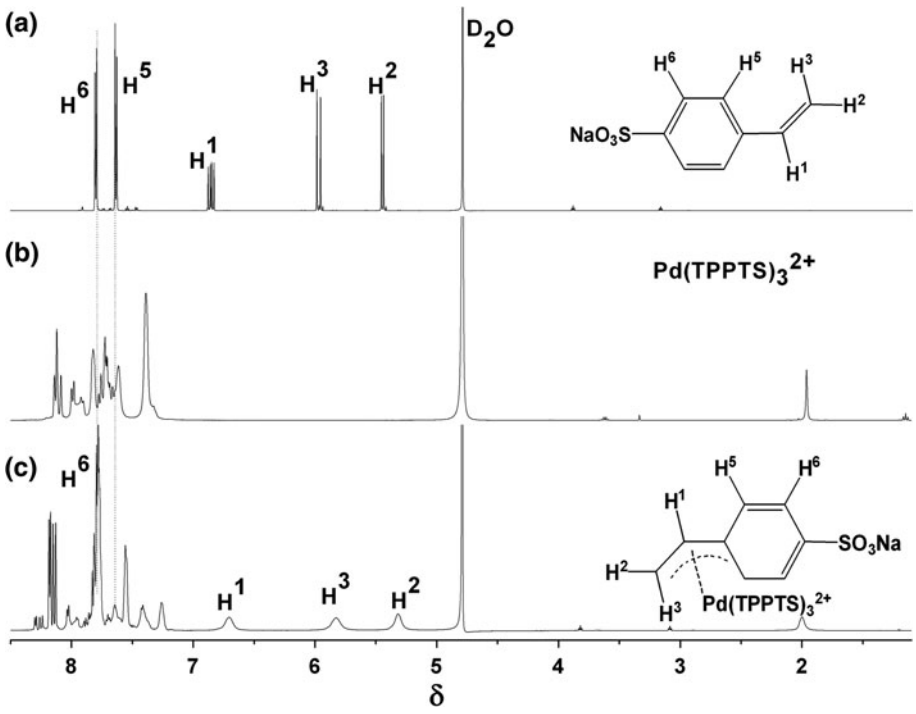


Fig. 4 ^{1}H NMR spectra of **a** sodium *p*-styrenesulfonate; **b** sodium *p*-styrenesulfonate in the presence of $Pd(TPPTS)_3^{2+}$ previously detected by ^{31}P NMR Reaction conditions: room temperature for 2 h, D_2O 1.0 ml, sodium *p*-styrenesulfate = 0.1 mmol, $Pd(OAc)_2$ = 0.02 mmol, P/Pd = 8, P_{CO} = 4 MPa

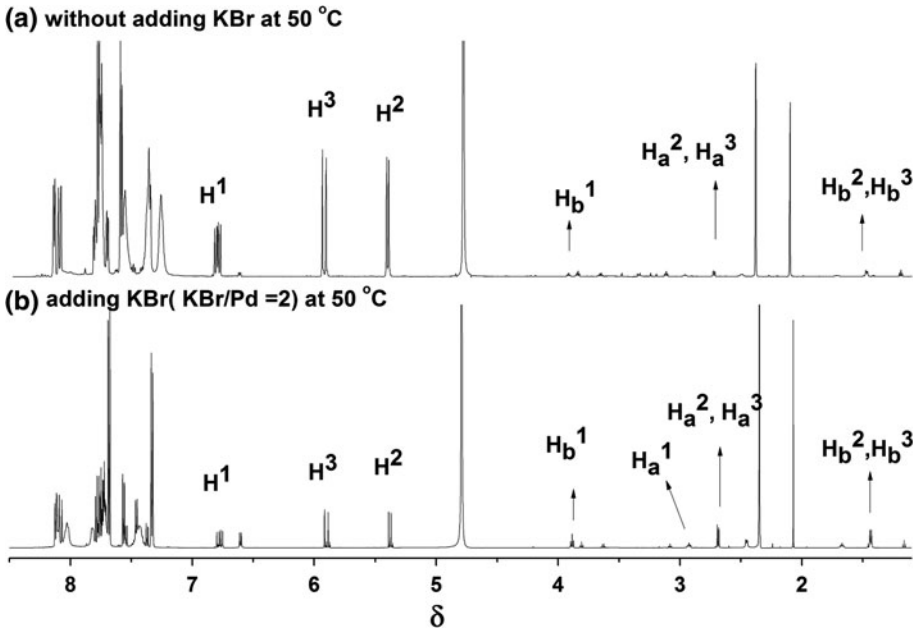


Fig. 5 ^{1}H NMR spectra of hydrocarboxylation of sodium *p*-styrenesulfonate in D_2O after reaction: **a** without any alkali metal halide; **b** adding KBr(the molar ratio of KBr/Pd=2). Reaction conditions: 50 °C for 2 h, D_2O = 1.0 ml, sodium *p*-styrenesulfonate = 0.1 mmol, $Pd(OAc)_2$ = 0.02 mmol, P/Pd = 8, *p*-TsOH = 0.1 mmol, P_{CO} = 4 MPa

4 Conclusions

The hydrocarboxylation of styrene catalyzed by water-soluble Pd-TPPTS complexes was investigated under different reaction conditions. Alkali metal halide salts can improve the yield of total acids and the selectivity towards 3-**PPA**. The selectivity of 3-**PPA** was increased in the order MCl < MBr < MI. From the spectra of ^{31}P NMR and ^{1}H NMR, it was found that alkali metal halide salts could stabilize the Pd(II) species, and styrene was coordinated and activated with Pd center even at room temperature, which implied the rate-limiting step for this reaction should be the following ones, like CO insertion or nucleophilic attack by H_2O. In the consideration of reaction activity and selectivity due to addition of alkali metal halide in hydrocarboxylation, the mechanism of the hydrocarboxylation catalyzed by Pd(II) and Pd(0) species was proposed.

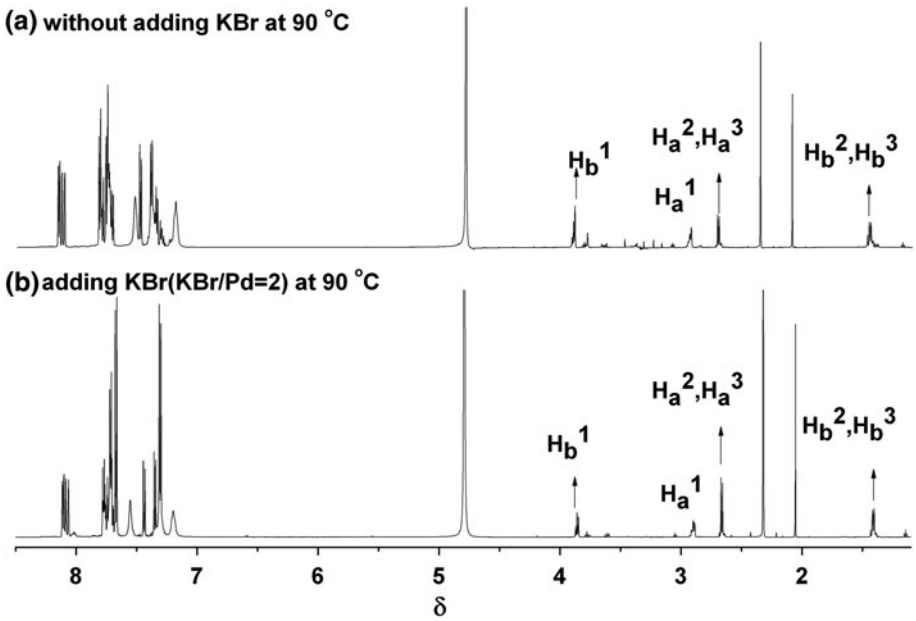
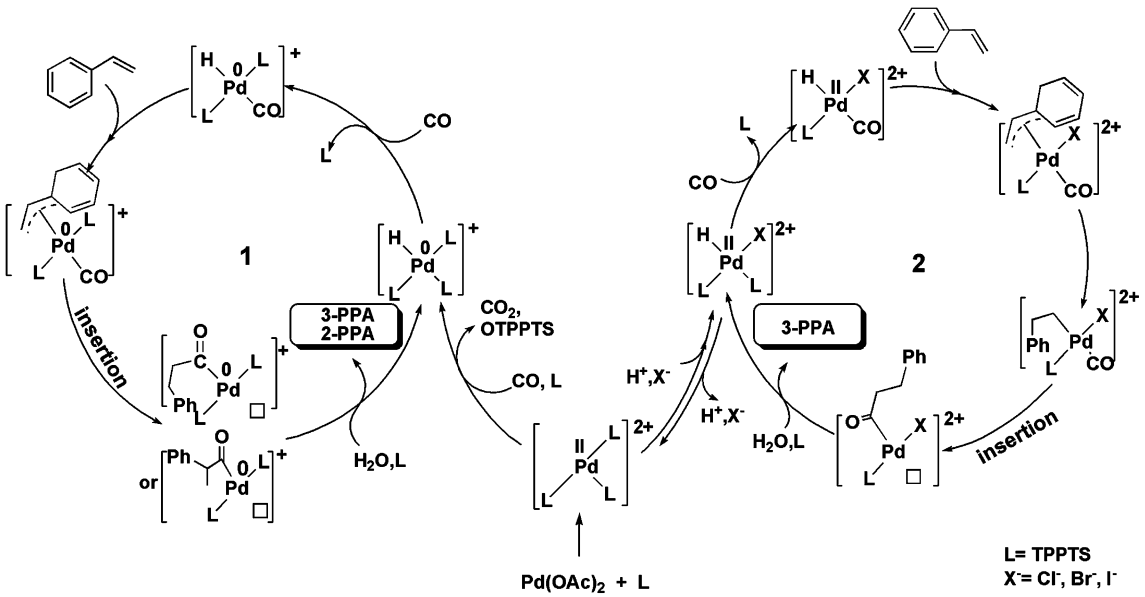


Fig. 6 ^{1}H NMR spectra of hydrocarboxylation of sodium *p*-styrenesulfonate in D_2O after reaction: **a** without any alkali metal halide; **b** adding KBr (the molar ratio of KBr/Pd=2). The reaction condition was the same as that in Fig. 5 except that higher reaction temperature (90 °C) was used



Scheme 3 The possible mechanism of hydrocarboxylation of styrene catalyzed by Pd(0) (**1**) and Pd(II) species (**2**), respectively

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