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Catalysis Today

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## Hydrocarboxylation of olefins by supported aqueous-phase catalysis

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### ARTICLE INFO

#### Article history:

Received 25 June 2014

Received in revised form 11 August 2014

Accepted 21 August 2014

Available online xxx

#### Keywords:

Acidic resin

1-Hexene

Styrene derivatives

Hydrocarboxylation

Supported aqueous phase catalysis

### ABSTRACT

Pd-TPPTS complexes supported on acidic macro-porous resins (Pd-TPPTS/resin) have been employed for the hydrocarboxylation of 1-hexene and styrene derivatives by supported aqueous phase catalysis (SAPC). Acidic macroporous resins acted as substitutes for both heterogeneous acids and supports of Pd-TPPTS complexes afforded many advantages, such as easy separation from organic products and good reusability. The prepared Pd-TPPTS/resin catalysts were characterized by FT-IR, TG, SEM and N<sub>2</sub> physisorption, which demonstrated that the Pd-TPPTS complexes were loaded on the resin. Compared with homogeneous analogue, the present SAP catalyst offered higher total acid yield and selectivity towards linear acid in the hydrocarboxylation of 1-hexene. Moreover, it was found that water had a significant influence on the catalytic activity and selectivity toward linear acid over the SAP catalyst. Optimum water/resin ratio at about 66.7% in the SAP catalyst afforded maximum activity under the given reaction temperature. The present SAP catalyst was highly Pd-leaching resistant and can be reused at least four times without obvious loss in activity.

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### 1. Introduction

The long-chain carboxylic acids through hydrocarboxylation of  $\alpha$ -olefin have a wide application in textile, agriculture and fine chemistry. On the other hand, ibuprofen, naproxen and ketoprofen which are used in pharmaceutical industry are synthesized catalytically by one-pot hydrocarboxylation of styrene derivatives. The catalytic process is an important issue and thus has attracted significant attentions in the worldwide [1,2]. The conventional catalysts involved Pd-P complexes in olefins hydrocarboxylation, especially for the Pd-TPP (triphenylphosphine), lots of publications have reported its high catalytic activity in this reaction [3]. Besides the TPP, other oil-soluble phosphine ligands such as cataCXium<sup>®</sup> A [4], diphosphine ligands [5–7] and chiral phosphine (S)-BNPPA and (R)-BNPPA [8] etc. were used in hydrocarboxylation with high catalytic activity.

The homogeneous Pd-phosphine complexes gave much higher activity in hydrocarboxylation; however, the difficulty in separation of Pd catalysts from organic products restricted the application

of these catalysts. To solve this problem, lots of methods were developed such as anchoring the Pd-P complexes onto supports [9,10], ossified the TPPTS (tri(*m*-sulfophenyl)phosphine) coordinated with Pd [11] and developed some biphasic catalysts etc. In the biphasic catalysis, TPPTS, one of the most famous water-soluble phosphine ligands, played an important role since it has been applied in the Ruhrchemie/Rhône-Poulenc oxo-process in 1984 [12]. Pd-TPPTS complexes were also widely used in hydrocarboxylation [13–17]. Except for TPPTS, the other water-soluble phosphine ligands such as dpppr-s [18,19], 2,7-bis(SO<sub>3</sub>Na)-Xantphos et [20] could be used in hydrocarboxylation of olefins with high activities.

Generally, the high activity of these Pd-phosphine complexes results from the promoter of Brønsted acids for forming Pd-H intermediates which are recognized as catalytic active species in the widely accepted Pd-H mechanism [15,19]. Thus, the Brønsted acid was employed as a necessary co-catalyst in olefins hydrocarboxylation. In general, homogeneous Brønsted acids, for example *p*-TsOH with weak coordination ability to Pd, were always used and gave high catalytic activities [21]. However, the utilization of these acids posed a corrosion problem. As a result, the homogeneous acids employed dramatically limit the development of the reaction, especially for industry application. To overcome this disadvantage, solid acid could be used as a replacement for the homogeneous acid

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with much less or without corrosion. Recently, our group has used solid acidic resin as Brønsted promoter and the carrier of Pd active catalysts which denoted as Pd-TPPTS-OTPPTS/Acidic resin catalyst in catalyzing hydroesterification of styrene derivatives; the catalysts showed excellent catalytic activities and selectivity for the branched esters [22].

Water not only acts as a reactant, but also a solvent in hydrocarboxylation of olefins [23]. In carboxylation of olefins, water-organic biphasic catalytic system provided a huge advantage over homogeneous catalysis in separating of noble metal complexes with organic products. The Rh-TPPTS complexes catalyst exhibited excellent catalytic activity and recyclability in the hydroformylation of propylene and butylenes in biphasic system [24]. However, the carbonylation of long chain olefins such as 1-hexene and 1-octene gave poor yield due to their poor solubility in water. Generally, to improve the mass transfer of these long chain olefins, surfactants such as CTAB, SDS and  $\beta$ -CD were widely employed in biphasic aqueous-organic catalytic system [25,26].

Supported aqueous-phase catalysis (SAPC) was another way to overcome the mass transfer limitations in organic reaction for the catalytic process occurring at the interface between the organic phase and the immobilized aqueous phase inside the pores of support materials. The SAPC combined the advantages of both biphasic and heterogeneous catalysis. Generally, the catalytic processes were performed in the aqueous phase, but the catalyst was utilized in a heterogeneous way. As a result, the SAPC exhibited the heterogeneous catalytic properties, such as easy separation and good reusability. Based on the unique feature, more attentions have been attracted in this highly effective catalytic process. It was widely used in organic reactions such as hydroformylation [27–29], atom transfer radical polymerization [30], Trost–Tsuji reaction [31] etc. However, to the best of our knowledge, the SAPC was rarely applied in hydrocarboxylation of olefins.

Based on our previous work [16,22], in this work, we utilized solid acids like acidic resin-supported Pd-TPPTS complexes to carry out hydrocarboxylation of olefins (including 1-hexene and styrene derivatives) by SAPC. Furthermore, the effects of reaction parameters on the catalytic performance and the reusability of the catalyst have been investigated.

## 2. Experimental

### 2.1. Materials

Pd(OAc)<sub>2</sub> was received by Sinopharm Chemical Reagent Co. Ltd. CO with a purity of >99.95% was provided by Beijing Longhui Jingcheng Gas Co., Ltd. TPPTS was purchased from Jintan Gaode Chemical Co., Ltd, China and recrystallized before uses. The <sup>31</sup>P NMR showed its purity >90%. 1-Hexene (98%) was obtained from Alfa Aesar. 4-Methylstyrene (96%) and 4-bromostyrene (98%) were obtained from J&K Chemicals; 4-*tert*-butylstyrene was provided by TCI. Acidic macro-porous resins were provided by Sunresin New Materials Co. Ltd., Xi'an, China, and Amberlist IR-120 and Amberlyst 15 were obtained from the Dow Chemical Company. All the resins were in the hydrogen form (–SO<sub>3</sub>H) and dry-type. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of N<sub>2</sub>.

### 2.2. Preparation of Pd-TPPTS/resin solid catalysts

The Pd-TPPTS/resin solid catalysts were prepared by incipient wetness impregnation method [22]. Prior to impregnation, the resins were washed with water and ethanol thoroughly to remove excess solvent, oligomers and other impurities until the solvent was colorless, and then dried at 90 °C for 16 h. The standard

procedures were conducted as follows: in a 100 ml round-bottom flask, Pd(OAc)<sub>2</sub> (0.0500 g, 0.22 mmol) and TPPTS (2.5 g, 4.4 mmol, the molar ratio of Pd to TPPTS was 1:20) were added into 12 ml of deoxygenated water, and the mixture was stirred for 1 h under N<sub>2</sub>. Subsequently, the solution of Pd-TPPTS complexes was injected to 10 g of the dry acidic LSI-600 resin under vacuum. Then the flask was held at the room temperature for 10 h under N<sub>2</sub>. Thereafter, the water was removed under vacuum and the 0.22% Pd-TPPTS/LSI-600 catalyst was obtained and stored under the protection of N<sub>2</sub>. Other catalysts including 0.10% Pd-TPPTS/LSI-600, 0.46% Pd-TPPTS/LSI-600, 0.22% Pd-TPPTS/Amberlyst 15, 0.19% Pd-TPPTS/LSCA-10, 0.18% Pd-TPPTS/LSCA-30 and 0.13% Pd-TPPTS/Amberlyst IR 120 were prepared in the similar procedures. The contents of Pd in all catalysts were determined by ICP-OES method.

### 2.3. Catalyst characterization

The as prepared Pd-TPPTS/resins catalysts were characterized by BET, TG, FT-IR and SEM. The physical properties of the resins and catalysts including surface area, pore volume and pore size distribution were determined by N<sub>2</sub> physisorption at 77 K on NOVA 2200, USA. The surface areas were calculated by Brunauer–Emmett–Teller (BET) method and the pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) model. The thermal stability of the LSI-600 resin and Pd-TPPTS/LSI-600 catalyst were tested on a Shimadzu DTG-50 apparatus under an Ar atmosphere (flow: 30 ml min<sup>−1</sup>) at a heating rate of 10 °C min<sup>−1</sup>. The FT-IR spectra were carried out in dispersed KBr pellets with a Nicolet 6700 FT-IR spectrometer. The surface morphology of the resin and catalysts were analyzed by SEM using a Bruker SUPRA 55VP with an acceleration voltage of 20 kV. Samples were gold coated prior to scanning. Pd leaching was determined by ICP-OES on a VISTA-PRO instrument.

### 2.4. Acid density determination

The acid densities of resins were determined by elemental analysis (S content) and titration method [32]. In the titration test, 0.2 g of resin was added into a sodium chloride aqueous solution (0.10 mol L<sup>−1</sup>, 50 ml). The mixture was stirred for 16 h at room temperature, followed that the solid was filtered off and washed with water (3 × 5 ml). The combined filtrate was titrated by a sodium hydroxide aqueous solution (0.08 mol L<sup>−1</sup>) using phenolphthalein as an indicator.

### 2.5. A typical procedure for hydrocarboxylation reaction over Pd-TPPTS/resins catalyst in supported aqueous phase

Olefins hydrocarboxylation catalyzed by Pd-TPPTS/LSI-600 in supported aqueous phase were performed in a 50 ml stainless-steel autoclave. In a standard procedure, 0.22% Pd-TPPTS/LSI-600 catalyst 1.5 g, deoxygenated water (1.0 g, 55.6 mmol), 1-hexene (0.5 g, 6.0 mmol) (*n*-undecane was used as internal standard for GC analysis) were added into the autoclave, then the reactor was sealed and flushed three times with 10 atm of CO. After that, the reactor was transferred into oil-bath, heated to the desired temperature (120 °C) and stirred for 6 h. Upon reaction completion, the autoclave was cooled with ice-water to room temperature and then vented slowly. The organic products and un-reacted olefins were extracted with 3 × 2 ml of heptane. The combined organic phase was dried by MgSO<sub>4</sub> and then used to be analyzed by GC and GC-MS. The solid catalyst was filtrated and then washed with 3 × 2 ml of heptane, followed by drying the catalyst at 75 °C for 5 h under vacuum condition. A fresh charge of reactants was introduced and the reaction was carried out as described previously. The hydrocarboxylation of styrene derivatives were carried out in similar

**Table 1**  
The physical properties of the resins and the Pd-TPPTS/resin catalysts.

Entries	Catalysts	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore diameter (nm)
1	LSI-600	42.4	0.17	19.1
2	Pd-TPPTS/LSI-600	22.1	0.10	15.2
3	LSCA-10	15.5	0.07	17.1
4	Pd-TPPTS/LSCA-10	9.3	0.01	14.7
5	LSCA-30	15.7	0.11	17.0
6	Pd-TPPTS/LSCA-30	10.3	0.03	15.0
7	Amberlyst 15	44.5	0.36	40.0
8	Pd-TPPTS/Amberlyst 15	27.1	0.14	15.9
9	Amberlyst IR 120	0.8	<0.001	–
10	Pd-TPPTS/Amberlyst IR 120	0.6	<0.001	–

procedures except for 2 ml of heptane was added as organic solvent during the reaction.

## 2.6. Hot filtration tests

To investigate whether the catalytic system underwent as a heterogeneous way in SAPC, hot filtration tests were carried out under the similar conditions as the previous hydrocarboxylation of 1-hexene and styrene, except for adding 2 ml of heptane as solvent for avoiding the unreacted 1-hexene adsorbed on solid catalyst in the case of 1-hexene as substrate. The Pd-TPPTS/resin catalyst was filtrated out from reaction mixture after 2 h (for 1-hexene) or 1 h (for styrene), giving 15.1% yield of total heptanoic acid and 19.5% yield of phenylpropanoic acid, respectively. Then the filtrate contained unreacted olefins continued to react in the reactor for another 4 h.

## 2.7. Water adsorption tests

The LSI-600 resin was dried under 90 °C for 16 h prior to the water adsorption measurement, and cooled to room temperature. Then, 1.00 g resin was immersed into water for a desired time at 25 °C. The resin was removed, and dried the water of the surface with a filter paper and then weighed.

## 3. Results and discussions

### 3.1. Characterization of Pd-TPPTS/acidic resin

The Pd-TPPTS/resin catalyst can be prepared by simple incipient wetness impregnation method and characterized by N<sub>2</sub> physisorption, TG, FT-IR, and SEM. Firstly, the physical properties of the resins and catalysts such as BET surface, pore distribution and pore volume were analyzed and the results are given in Table 1. From the Table 1, the BET surface area and mean pore volume of the resins were decreased remarkably after the Pd-TPPTS complexes loaded, indicating the Pd-TPPTS complexes were loaded into inner surface of the macro-porous resins.

In the next step, the thermal stability of the resin and corresponding catalysts were examined. All resins-supported catalysts showed a very similar tendency. The LSI-600 resin and Pd-TPPTS/LSI-600 catalyst were exemplified and the TGA curves are given in Fig. 1. The weight loss around 120 °C was the losing of physically adsorbed water in the curves of both resin and catalyst. When the temperature increased to 260 °C, the resin started to lose weight, indicating the loss of –SO<sub>3</sub>H group from the resin [33]. As for the Pd-TPPTS/LSI-600 catalyst, this temperature increased to 288 °C, and this may be due to the weak interaction between the Pd-TPPTS complexes and resin. The mass loss over 400 °C was attributed to the decomposition of the resin framework [33]. The TG curves also indicated that both the supported catalyst and resin were thermally stable under the reaction temperature (<150 °C), which was in agreement with our previous result [22].

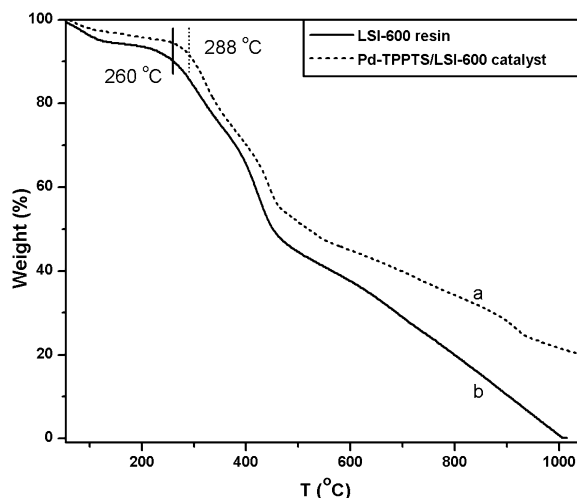


Fig. 1. TG curves of the (a) Pd-TPPTS/LSI-600 catalyst and (b) LSI-600 resin.

The FT-IR spectra are shown in the Fig. 2. In Fig. 2a, the spectrum of LSI-600 Resin, the weak peaks at 1412–1643 cm<sup>-1</sup> were ascribed to the vibrations of C–H groups in the substituted benzene ring skeleton. The other weak peaks at 673–916 cm<sup>-1</sup> were attributed to the out-of-plane bending vibrations of C–H groups in the substituted benzene styrene ring, respectively. The peaks at 1125 and 1039 cm<sup>-1</sup> were assigned to the symmetric and asymmetric stretching vibrations of –SO<sub>3</sub><sup>-</sup> group, respectively [34]. In Fig. 2b, the spectrum of Pd-TPPTS complexes, the peaks were appeared nearly at the same places to the LSI-600 resin for they

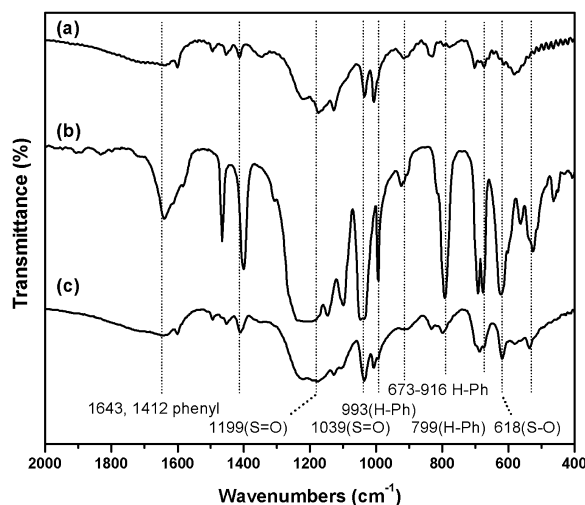
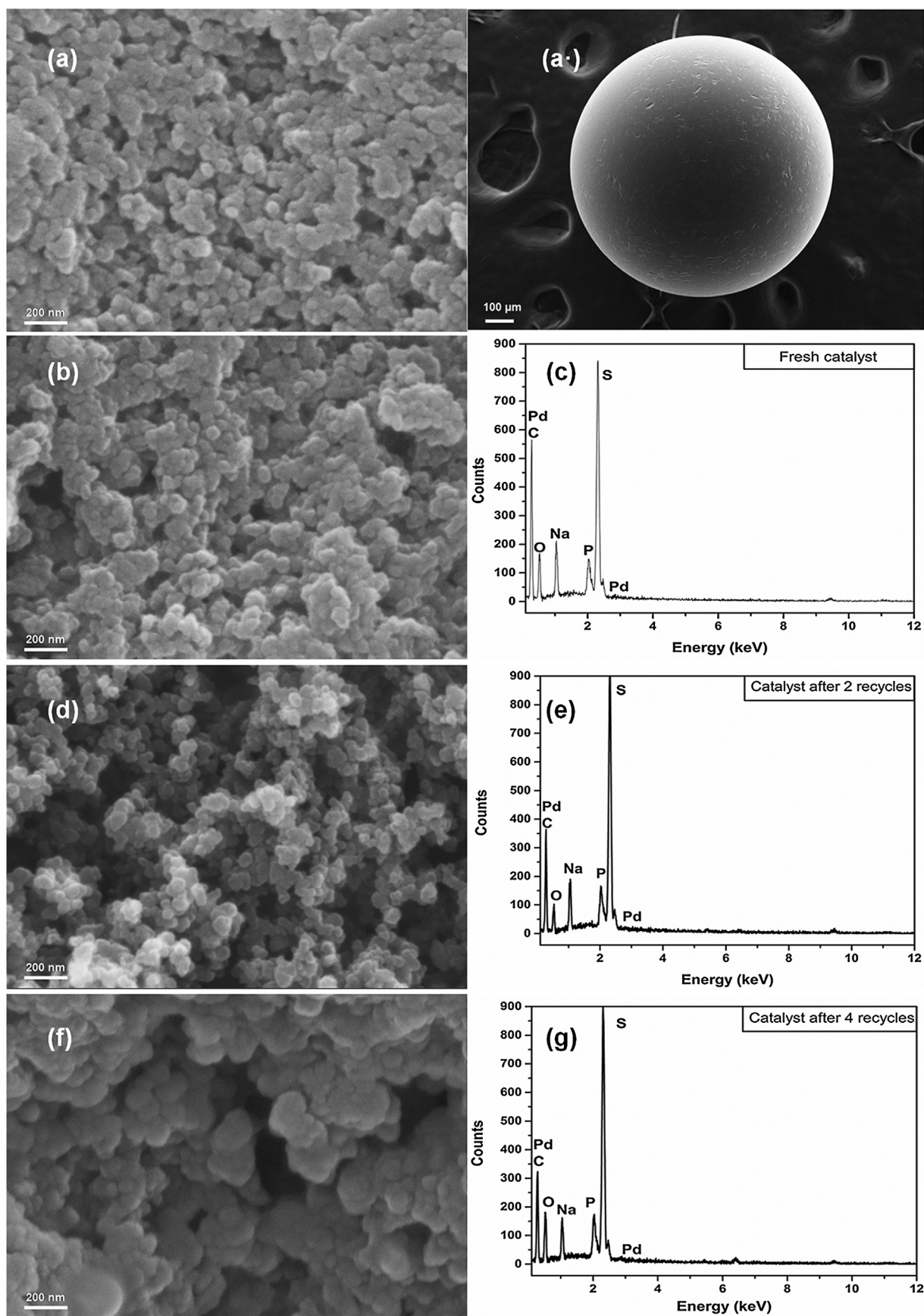


Fig. 2. FT-IR spectra of (a) LSI-600 resin, (b) Pd-TPPTS complexes and (c) Pd-TPPTS/LSI-600 catalyst.





**Fig. 3.** SEM image of (a) LSI-600 resin, (a') LSI-600 resin (scale bar: 100 μm), (b) the fresh Pd-TPPTS/LSI-600 catalyst, (d) the Pd-TPPTS/LSI-600 catalyst after 2 recycles, (f) the Pd-TPPTS/LSI-600 catalyst after 4 recycles (scale bar in a, b, d and f: 200 nm), and EDX spectrum of (c) the fresh Pd-TPPTS/LSI-600 catalyst, (e) the Pd-TPPTS/LSI-600 catalyst after 2 recycles and (g) the catalyst after 4 recycles.

**Table 2**  
Surface composition of the catalyst after 4 recycles detected by EDX.<sup>a</sup>

Catalysts	Surface mass concentration (wt%)					
	C	S	P	Na	O	Pd
Fresh Pd-TPPTS/LSI-600	55.6	15.8	2.16	4.02	22.2	0.22
Catalyst after 2 recycles	58.0	19.3	2.6	4.6	15.3	0.21
Catalyst after 4 recycles	50.1	18.0	2.8	3.2	25.6	0.28

<sup>a</sup> The mean error in surface concentration was about  $\pm 0.5\%$ .

have the similar groups such as phenyl- and  $\text{SO}_3^-$ . In the Fig. 2c, the Pd-TPPTS/LSI-600 catalyst, compared to the former LSI-600 and Pd-TPPTS complexes, some peaks of Pd-TPPTS complexes could be found in this spectrum, for example, peaks at 618, 1096  $\text{cm}^{-1}$  were attributed to symmetric and asymmetric stretching vibrations of  $-\text{SO}_3^-$  group and 789, 993  $\text{cm}^{-1}$  were assigned to vibrations of C–H groups [34]. The results indicated further that the Pd-TPPTS complexes have been loaded on the LSI-600 resin.

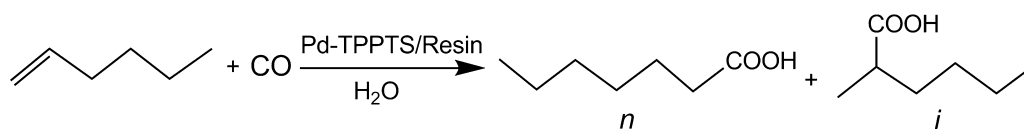
The morphologies of the LSI-600 resin, the fresh Pd-TPPTS/LSI-600 catalyst and the spent catalysts were presented by SEM photographs. As shown in Fig. 3, it could be seen that the catalyst had a good stability during the reaction. At first, the fresh Pd-TPPTS/LSI-600 catalyst had a similar morphology with the LSI-600 resin (Fig. 3b vs a). In addition, the morphology of the catalyst after 2 recycles was very similar to that of the fresh catalyst (Fig. 3d vs b) although the spent catalysts exhibited a much rougher surface. These results indicated the supported Pd-TPPTS/LSI-600 catalysts were highly stable under the reaction condition. The EDX spectra of the fresh catalyst, the spent catalysts were also analyzed and the results are given in Fig. 3. The intensity of peaks for Pd was weak due to the low loading amount. However, the peak attributed to P was rather high, indicating the TPPTS was loaded on the resin. Moreover, the EDX spectra showed that the surface compositions of Pd or P did not change significantly even after 4 recycles (Table 2), indicating the TPPTS and Pd species in the present catalyst was highly leaching-resistant.

### 3.2. Catalytic performances of Pd-TPPTS/acidic resins in hydrocarboxylation of 1-hexene

1-Hexene was chosen as substrate for hydrocarboxylation (Scheme 1). Besides the carboxylic acid products, minor amounts of polymer and isomer from 1-hexene were also found. At first,

various acidic resins were employed as Brönsted acid promoters and supports of Pd-TPPTS complexes in hydrocarboxylation of 1-hexene in the SAPC system, and the results are given in Table 3. When the resin was absent, in the Pd-TPPTS-*p*-TsOH catalyst system, the yield of total acids was only 20.6% in the molar ratio of 2.5 (14.7% of heptanoic acid and 5.9% of 2-methylhexanoic acid), meanwhile, polymer was found (Table 3, entry 1). However, the acidic macro-porous resin-supported catalysts such as Pd-TPPTS/LSI-600, Pd-TPPTS/LSCA-10, Pd-TPPTS/LSCA-30 and Pd-TPPTS/Amberlyst 15 afforded the total acid yields of 88.3% with the *n/i* about 4.5, 81.2% with the *n/i* about 3.7, 75.8% with the *n/i* about 4.3, and 78.2% with the *n/i* about 4.1, respectively (Table 3, entries 2–5). The small differences in yield and *n/i* were probably because of the different properties of the resins (Table 1). In contrast, the Pd-TPPTS/Amberlyst IR 120 catalyst, a gel-type acidic resin (Amberlyst IR 120) without any pore supporting Pd-TPPTS complexes, gave a rather low activity in catalyzing 1-hexene hydrocarboxylation (Table 3, entry 6). This was probably because the catalytic active Pd-TPPTS complexes and water were mainly adsorbed the outer surface of the resin and might tend to aggregate, which afforded poor activity for hydrocarboxylation of 1-hexene. In this case, minor amounts of polymer have been detected, likely resulting from 1-hexene polymerization. The results demonstrated clearly that porosity of acidic resins played a crucial role in hydrocarboxylation of 1-hexene, and moreover the acidic resin-supported Pd-TPPTS/LSI-600 catalyst could offer higher *n/i* molar ratio than that of Pd-TPPTS-*p*-TsOH (Table 3, entries 1 vs 2–5).

Apart from the resin support, the reaction conditions including CO pressure, molar ratio of P/Pd and Pd loading could influence the catalytic activity and the molar ratio of *n* acid to *i* acid. As shown in Table 4, it can be seen that the pressure of CO has a great influence on the reaction. The acids yield increased with increasing the CO pressure. For instance, when the CO pressure was 1.5 MPa, the total acids yield was 25.8% (17.9% of *n*, 5.0% of *i* and 2.9% of other acids); the yields increased to 88.3% when the CO pressure was 3.5 MPa (Table 4, entries 1–3). Aside from the CO pressure, the P/Pd molar ratio had also a great effect on the reaction. For example, when the P/Pd was 5, no acid product was detected (Table 4, entry 5), and the palladium black was observed after the reaction. However, when the P/Pd was increased to 20, the acids yield reached to 88.3% (Table 4, entry 3). The optimal P/Pd in the present catalyst system was higher than conventional homogeneous catalyst which was always only 4/1 in agreement with the expected maximum



**Scheme 1.** Hydrocarboxylation reaction of 1-hexene.

**Table 3**  
Effect of various acidic resins as supports on hydrocarboxylation of 1-hexene.<sup>a</sup>

Entries	Catalysts	Acid density <sup>b</sup> (mmol g <sup>-1</sup> )	GC yield (%)			<i>n/i</i> <sup>d</sup>
			<i>n</i>	<i>i</i>	Others acids <sup>c</sup>	
1 <sup>e</sup>	Pd-TPPTS- <i>p</i> -TsOH	–	14.7	5.9	–	2.5
2	Pd-TPPTS/LSI-600	1.71	64.2	14.3	9.8	4.5
3	Pd-TPPTS/LSCA-10	2.57	56.8	15.4	9.0	3.7
4	Pd-TPPTS/LSCA-30	3.33	54.7	12.7	8.4	4.3
5	Pd-TPPTS/Amberlyst 15	4.30	55.3	14.0	8.9	4.1
6	Pd-TPPTS/Amberlyst IR120	2.45	–	–	–	–

<sup>a</sup> Reaction conditions: CO pressure 3.5 MPa, 100 °C, 1-hexene 6 mmol, olefins/Pd = 200 (molar ratio), 6 h, P/Pd = 20, deoxygenated H<sub>2</sub>O 1.0 ml.

<sup>b</sup> The acid density of the support were determined by the titration method given in the experimental part.

<sup>c</sup> Other acid was mainly 2-ethylpentanoic acid.

<sup>d</sup> The molar ratio of heptanoic acid (*n*) to 2-methylhexanoic acid (*i*).

<sup>e</sup> Pd-TPPTS-*p*-TsOH catalyst, 5 ml water, and 0.3 g *p*-TsOH were added as Brönsted acid promoter.

**Table 4**  
The hydrocarboxylation of 1-hexene by supported aqueous catalyst of Pd-TPPTS/LSI-600 under different reaction conditions.<sup>a</sup>

Entries	P <sub>CO</sub> MPa	P/Pd <sup>b</sup>	Pd loading (wt% <sup>c</sup> )	GC yield (%) <sup>d</sup>			n/i <sup>f</sup>
				n	i	Other acids <sup>e</sup>	
1	1.5	20	0.21	17.9	5.0	2.9	3.6
2	2.5	20	0.21	37.5	8.9	5.8	4.2
3	3.5	20	0.21	64.2	14.3	9.8	4.5
4	4.5	20	0.21	62.6	15.3	9.7	4.1
5	3.5	5	0.21	–	–	–	–
6	3.5	10	0.21	15.3	3.6	2.4	4.2
7	3.5	15	0.21	33.4	7.3	5.1	4.6
8	3.5	20	0	–	–	–	–
9	3.5	20	0.10	29.6	7.6	4.6	3.9
10	3.5	20	0.46	63.7	15.5	9.9	4.1

<sup>a</sup> Reaction conditions: 1-hexene 6 mmol, 1-hexene/Pd = 200 (molar ratio), water 1.0 ml, 120 °C, 6 h.

<sup>b</sup> Molar ratio of TPPTS/Pd.

<sup>c</sup> Pd loading amount were detected by ICP-OES.

<sup>e</sup> Other acid was mainly 2-ethylpentanoic acid.

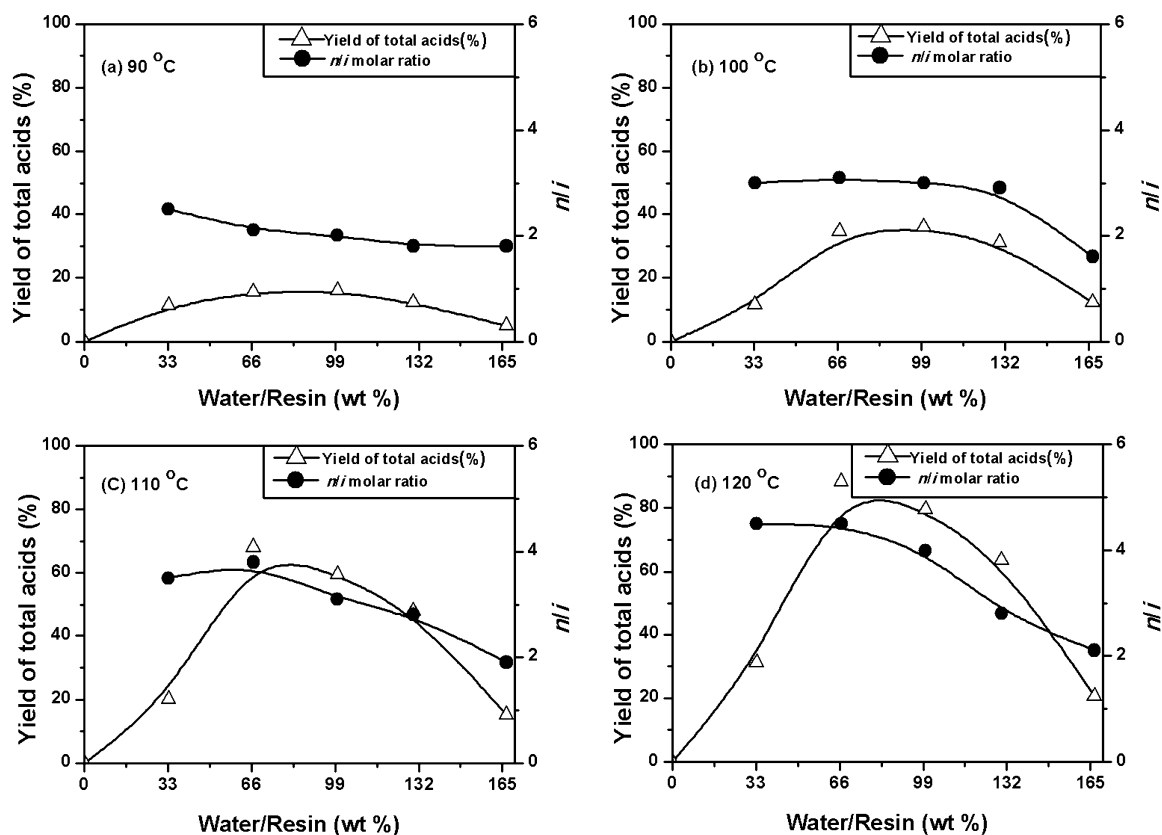
<sup>f</sup> The molar ratio of heptanoic acid (n) to 2-methylhexanoic acid (i).

coordination number. Although the definite reason for the stabilizing effect of the higher P/Pd was currently unknown, it might be related to dynamic equilibrium among active Pd species affected by the present reaction conditions. In addition, Pd species was essential for this reaction, no acid product was obtained in the absence of Pd complex (Table 4, entry 8). Increasing Pd loading (less than 0.21%) could promote the reaction, for example, total yield of acids improved from 41.8% to 88.3% when Pd loading increased from 0.10% to 0.21% (Table 4, entries 8, 9 and 3). However, the acids yield

increased only slightly when the Pd loading was more than 0.21% (Table 4, entries 3 and 10).

In SAPC, water has a remarkable influence on the catalytic performances. The large amount of water induced that the reaction was carried out as in a conventional biphasic system. On the contrary, however, the small amount of water was only absorbed on the solid support but not form a thin aqueous film [35,36]. In this aspect, a suitable amount of water can not only act as a reactant but also fix the Pd-TPPTS complexes effectively onto the surface of resin. On the basis of the above consideration, the influence of water content on the hydrocarboxylation of 1-hexene catalyzed by Pd-TPPTS/LSI-600 was explored and the results are shown in Fig. 4. It was demonstrated that the water amount had great influences on the total acid yield and n/i ratio at different temperatures. The total acid yield increased with water content initially but dropped down when more water was introduced at given reaction temperature. It was noteworthy that when the temperature increased, the yield of total acid increased under the given amount of water. For example, the yield increased from 12.2% to 64.3% with raising temperature from 90 °C to 120 °C when the ratio of water to resin was kept at 130%. Meanwhile, the n/i increased with the temperature ranged from 60 °C to 120 °C. It was observed that the highest acid yield was obtained when the water/resin ratio was 66.7% in 1-hexene hydrocarboxylation.

To further investigate the effect of water content on the catalytic performances, we examined the water absorption on LSI-600 resin under room temperature. As shown in Fig. 5, the water absorption was very fast on the LSI-600 resin and saturated water absorption happened at water/resin = 162%. It was expected that the amount of water should not be too low which would provide only a small film on the support and not be too high to prevent pore plugging which restricts diffusion of the reactants or prevents catalyst leaching.



**Fig. 4.** The dependence of water content on catalytic performances under different temperature: (a) 90 °C, (b) 100 °C, (c) 110 °C and (d) 120 °C. (Δ) Yield of total acids (%), (●) n/i molar ratio. Reaction conditions: 0.22% Pd-TPPTS/LSI-600 (1.5 g), 1-hexene (0.5 g, 6.0 mmol), 1-hexene/Pd = 200 (molar ratio), 6 h, 3.5 MPa.



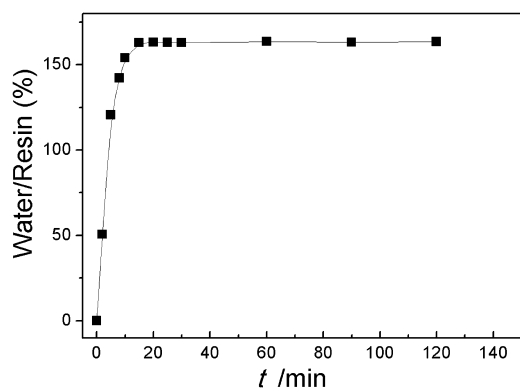


Fig. 5. The water absorption of LSI-600 resin (25 °C).

The optimum water content which gave the highest performance of the SAP catalyst depended on the type and properties of the supports, the water solubility of the reactants or the liquid–liquid mass transfer rate and the catalyst precursor system. In the present work, Pd-TPPTS/LSI-600 catalyst could afford the highest acid yield at water/resin about 66.7% in hydrocarboxylation of 1-hexene. On the other hand, it was observed that  $n/i$  decreased with increasing water content at temperature from 90 °C to 120 °C. Because the porosity of resin was favorable for enhancing the selectivity toward  $n$  acid likely due to the steric effect (Table 3, entries 1 vs 2–5), the more addition of water resulted in greater mobility of Pd-TPPTS complexes, and thus decreasing selectivity in nearly biphasic condition. Indeed, it has been reported that the optimal activities in SAPC are obtained for fully filled pore volume materials in hydroformylation [37]. However, in the present catalyst system, the optimal amount of water (water/resin was 66.7%) was more than that of fully filled pore volume materials (water/resin was about 10%). This was because that the temperature in hydrocarboxylation of 1-hexene was much higher than that of the previous report (50 °C), resulting in more water to evaporate and exist in vapor phase, and moreover, the water was acted as a reactant and consumed in the hydrocarboxylation. Thus the more water was needed to introduce into the reaction.

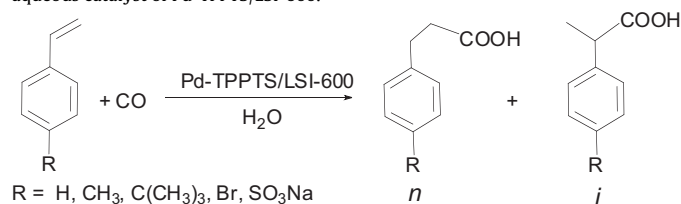
### 3.3. The generality and reusability of the Pd-TPPTS/resin catalyst in SAPC

To extend the application of the present catalyst, styrene derivatives were used as substrates and reacted with CO and water to produce corresponding acids, and the results are given in Table 5. The reaction conditions in styrene derivatives were the same as that of 1-hexene, except for adding 2 ml of heptane as organic solvent since the aromatic olefins were easy to polymerize in the absence of any other solvent.

From the Table 5, it could be found that good yields were shown in the hydrocarboxylation of styrene derivatives catalyzed by Pd-TPPTS/LSI-600 catalyst in SAP under the given conditions. For example, in the styrene hydrocarboxylation, 39.3% and 32.8% yield of 3-phenylpropanoic acid and 2-phenylpropanoic acid were obtained. However, the yield of acid products decreased dramatically (only 10.6% and 6.4% yield of  $n$  and  $i$  acids) in the absence of heptane (Table 5, entry 2). As for the 4-bromostyrene, equimolar of  $n$  and  $i$  acids (27.6% yield) were obtained. Meanwhile, 33.5% yield of  $n$  acid and 25.8% yield of  $i$  acid, and 45.0% yield of  $n$  acid and 28.1% yield of  $i$  acid were obtained in hydrocarboxylation of 4-*tert*-butylstyrene and 4-methylstyrene, respectively (Table 5, entries 4 and 5). If water-soluble aromatic olefin was employed in hydrocarboxylation catalyzed by Pd-TPPTS/LSI-600 in SAPC, over 99% of yield can be achieved (Table 5, entry 6). Compared with

Table 5

The hydrocarboxylation of styrene and its derivatives catalyzed by supported aqueous catalyst of Pd-TPPTS/LSI-600.<sup>a</sup>



Entry	R	GC yield (%)		$n/i^b$
		$n$	$i$	
1	H	39.3	32.8	1.2
2 <sup>c</sup>	H	10.6	6.4	1.7
3	Br	27.6	27.6	1.0
4	C(CH <sub>3</sub> ) <sub>3</sub>	33.5	25.8	1.3
5	CH <sub>3</sub>	45.0	28.1	1.6
6 <sup>d</sup>	SO <sub>3</sub> Na	55.2	43.8	1.3

<sup>a</sup> Reaction conditions: catalyst 1.5 g, olefins/Pd=200, H<sub>2</sub>O 1 ml, heptane 2 ml, 100 °C, 5 h.

<sup>b</sup> The molar ratio of  $n$  acid to  $i$  acid.

<sup>c</sup> No heptane was added in the reaction.

<sup>d</sup> Detected by <sup>1</sup>H NMR in D<sub>2</sub>O.

other oil-soluble styrene derivatives, the water-soluble sodium 4-vinylbenzenesulfonate had the highest activity in the hydrocarboxylation due to the fact that the latter olefin had high solubility in water, mass transfer limitation could be overcome and the much higher catalytic activity could be achieved.

One of the most important properties of heterogeneous catalyst is the reusability. The recyclability of the acidic macro-porous resin supporting Pd-TPPTS complexes catalyst is shown in the Fig. 6. The catalyst could be reused at least four times without obvious loss of activity; meanwhile, the  $n/i$  molar ratio was constant in consecutive catalytic cycles. To further investigate the amount of Pd leaching into the solvent after the reaction, the solvent was analyzed by ICP-OES. It was found that there was very low leaching of Pd into the organic products. For the first run, the Pd leached into the organic phase was only 0.9 ppm, and in the third run was 1.2 ppm. These results demonstrated that the Pd leaching could be negligible for the catalytic reaction. The observation suggested that Pd-TPPTS/LSI-600 catalyst had good reusability in catalyzing hydrocarboxylation of 1-hexene. To investigate whether the present catalyst was performed in a heterogeneous manner, hot filtration tests were carried out and the results are summarized in

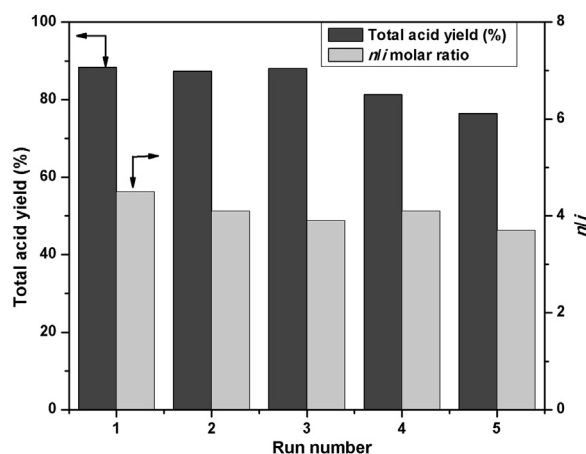
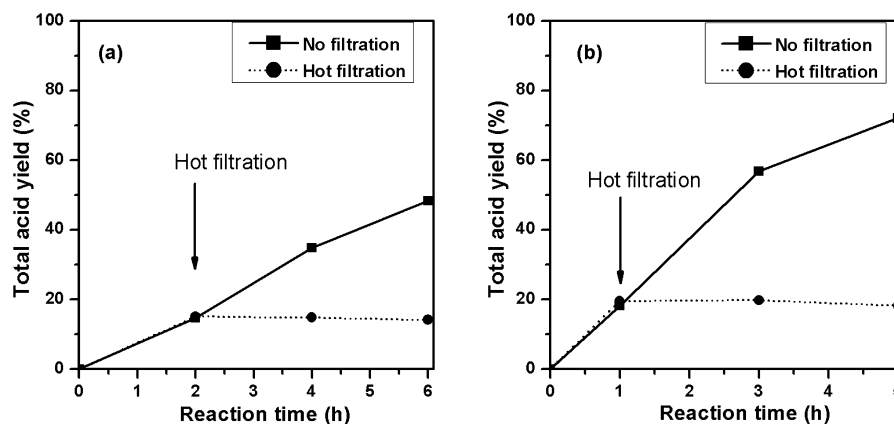


Fig. 6. Recycling of the supported aqueous catalyst of Pd-TPPTS/LSI-600 in 1-hexene hydrocarboxylation.



**Fig. 7.** Hot filtration tests for the supported aqueous catalyst of Pd-TPPTS/LSI-600 in hydrocarboxylation of 1-hexene (a) and styrene (b). Reaction conditions: substrate (6.0 mmol), substrate/Pd = 200 (molar ratio), 120 °C, hexane 2 ml, water 1.0 g, catalyst 1.5 g; reaction temperature was 100 °C for hydrocarboxylation of styrene.

**Fig. 7.** In the hot filtration of 1-hexene hydrocarboxylation, 2 ml of hexane was added to avoid the unreacted olefins to be absorbed on the resins. From the Fig. 7, it could be seen that both in the hydrocarboxylation of 1-hexene and styrene, after the hot filtration, no additional acids were formed. The results of hot filtration indicated that the Pd-TPPTS/LSI-600 catalyzed hydrocarboxylation of olefins in a heterogeneous way.

#### 4. Conclusion

In summary, a facile preparation of heterogeneous catalyst Pd-TPPTS complexes supported onto acidic resin LSI-600, Pd-TPPTS/LSI-600, was achieved in catalyzing hydrocarboxylation of 1-hexene and styrene derivatives, CO and water in SAPC with high efficiency and activity. It was found that 88.3% yield of heptanoic acid and 2-methylhexanoic acid was obtained in hydrocarboxylation of 1-hexene under organic solvent free conditions. Meanwhile, the amount of water added had a great effect on the catalytic activity. The present catalyst could be also extended for hydrocarboxylation of styrene derivatives with high selectivity. The hot filtration tests showed the Pd-TPPTS/LSI-600 catalyst was carried out in a heterogeneous way and it could be reused at least four times without remarkable loss in activity.

#### Acknowledgements

The authors are grateful for support from the National Natural Science Foundation of China (U1179302, 21373082) and One Hundred Person Project of the Chinese Academy of Sciences.

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