

# Selective aerobic oxidation of styrene to benzaldehyde catalyzed by water-soluble palladium(II) complex in water

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Selective oxidation of styrene to benzaldehyde has been carried out for the first time in aqueous phase by using a green and water-soluble palladium(II) complex as a catalyst under neutral, chloride and base-free conditions. The influences of reaction temperature, reaction time, palladium concentration and O<sub>2</sub> pressure on the conversion of styrene and the selectivity to benzaldehyde have been discussed. The reaction products, benzaldehyde, benzoic acid, acetophenone are readily isolated by ether extraction at room temperature. The water-soluble catalyst immobilized in aqueous phase can be reused for eight catalytic runs with an almost constant catalytic activity for the styrene oxidation. The influence of substituting groups in the aromatic ring of styrene on the reactivity was also discussed. Spectroscopic studies revealed that the hydrophilic dipyrindyl-based ligand (**L**) with Pd(OAc)<sub>2</sub> formed a water-soluble Pd(II) complex. The UV/Vis spectra analysis further showed that the Pd(II)-**L** complex could serve as the catalytically active species in the present catalytic system.

## Introduction

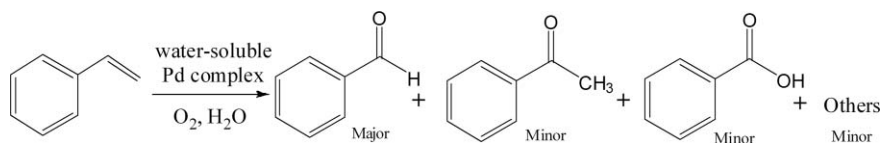
Today, in the chemical process, traditional organic solvents are used in large quantities, which has led to various environmental and health concerns. As part of green chemistry efforts, a variety of cleaner solvents have been evaluated as replacements.<sup>1</sup> As an alternative solvent, water has been paid extraordinary attention because it is not only inexpensive and environmentally benign, but also shows unique reactivity and selectivity that cannot be obtained in organic solvents.<sup>2</sup> Furthermore, it could offer the easy approach for separation of organic reagents or catalysts from aqueous phase. Thus, the development on an organic catalytic reaction using water as reaction medium has attracted much more attention. By far, the types of organic reactions in water are now as diverse as those in organic solvents.<sup>3</sup> Especially, many oxidation reactions using molecular oxygen as oxidant have been carried out in water, which is much safer than in organic solvents. One of the limitations of water as reaction medium is the low solubility of some gases and many organic compounds in water. Moreover, many catalysts are insoluble in water and could be sensitive to water, which also limit the widespread application of water.<sup>4</sup> Thus many strategies, including adding cosolvent or surfactant, designing water-soluble catalyst, *etc.*, are employed to circumvent these problems.<sup>5</sup> As a classic example of water-soluble catalyst application, Sheldon *et al.* have designed a water-soluble bathophenanthroline disulfonate (PhenS\*) ligand coordinating with palladium acetate for aerobic oxidation of olefins or alcohols in aqueous phase.<sup>6</sup> Buffin

*et al.* also utilized a water-soluble Pd(II)-biquinoline catalyst for the aerobic oxidation of alcohols.<sup>7</sup>

The water-soluble polymer poly(ethylene glycol) (PEG) is known to be inexpensive, thermally stable, nontoxic, nonvolatile, and recoverable media for catalysis.<sup>8</sup> In particular, it was reported that adding PEG in water as a cosolvent will lead to an apparent decrease of the aqueous solution polarity, then the consequent increase in solubility of organic molecules.<sup>9</sup> Furthermore, the use of PEG as the supports has attracted particular attention because of the easy recovery of the catalyst/ligand and attractive catalytic performance of the resultant catalysts. More recently, PEG-supported Pd catalyst has been successfully used in many reactions, including oxidation reactions,<sup>10</sup> but Pd catalysts always suffer from deactivation due to the formation of palladium black. Therefore, the bidentate nitrogen ligands have been applied to stabilize efficiently palladium(II) or (0) active species.<sup>11</sup> However, to the best of our knowledge, there is no previous report of PEG anchoring bidentate dipyrindyl ligand to form a water-soluble palladium(II) complex as a catalyst employed for aerobic oxidation in water.

Olefin oxidation is an important transformation in the production of fine chemicals. Metal-catalyzed oxidation of olefins can give rise to a whole variety of organic products,<sup>12</sup> for example, the well known Wacker-type oxidation converts terminal olefins to methyl ketones. Besides, olefins can also be converted into aldehydes by the cleavage of C=C double bond using some specific catalysts, such as OsO<sub>4</sub>-oxone, Au(I)-neocuproine complex, iron-salen complex and [cis-Ru(II)(dmp)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (dmp = 2,9-dimethylphenanthroline).<sup>13</sup> Alternatively, He *et al.* have employed PdCl<sub>2</sub> as catalyst for the oxidation of styrene in scCO<sub>2</sub>/PEG biphasic catalytic system, and they obtained the moderate selectivity for benzaldehyde.<sup>14</sup> Sigman and Cornell have also observed the cleavage of C=C double bond and the

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**Scheme 1** Aerobic oxidation of styrene catalyzed by water-soluble Pd(II) complex in aqueous phase.

formation of aldehyde by using Pd(II) N-heterocyclic carbene complex as a catalyst for olefin oxidation in THF.<sup>15</sup>

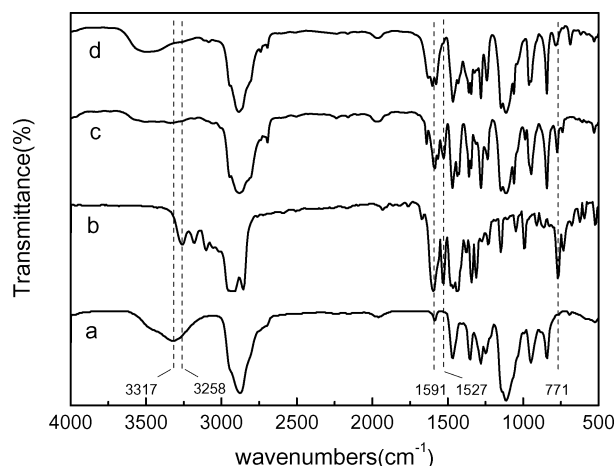
Although Wacker-type oxidation has been performed in water with Pd(II) catalysts in combination with copper salt (CuCl) under aerobic conditions,<sup>16</sup> decreased atom economy due to by-products caused by chlorination, the erosion of metallic reactors and more-complicated product isolation associated with these reactions limit large-scale applications. Consequently, the development of a simple, efficient and environmentally benign method for olefin oxidation is still of great challenge. Herein, we described the design and synthesis of the dipyriddy ligand anchored on PEG and its ability to form a water-soluble Pd(II) complex as a sole catalyst for the aerobic oxidation of styrene in water. We expected the long chains of PEG could not only enhance the solubility of substrate in water, but also anchor the palladium(II) species in the water phase. A combination of palladium acetate and PEG-anchoring bidentate dipyriddy ligand in water afforded different oxygenation products of styrene, but benzaldehyde was obtained as a main product using the present catalyst (Scheme 1). Although the oxidation of styrene has been reported previously, no cleavage of the C=C double bond of styrene was investigated in detail in the aqueous phase until now. This work also provides a new route of styrene oxidation under neutral, chloride and base-free aqueous conditions.

## Results and discussion

### Catalyst preparation and characterization

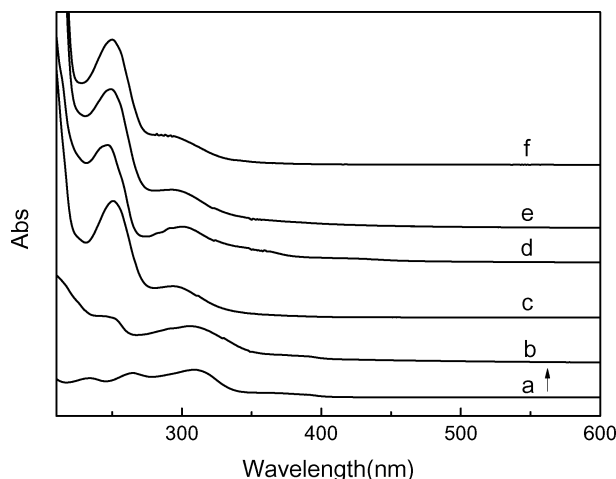
The functionalized PEG (**L**) was synthesized by covalent attachment of 2,2'-dipyriddyamine to the tip of PEG in two steps. PEG-2000 was first quantitatively converted to PEG dimesylate in a similar way as described in Ref.<sup>17</sup> Then attachment of 2,2'-dipyriddyamine with PEG dimesylate in the presence of sodium hydride afforded **L** which was isolated and purified by column chromatography. In the next step, the catalyst solutions were prepared by coordinating Pd(OAc)<sub>2</sub> with **L** overnight in water, and finally, a clear yellow-orange solution was obtained.

The preparation processes were monitored and confirmed with NMR, FTIR and UV/Vis analyses. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **L** indicated the presence of pyridyl groups, oxyethylene units; the resonance of the methylene protons CH<sub>2</sub>N as a triplet at 4.32 ppm confirmed the covalent linkage of 2, 2'-dipyriddyamine to the tip of PEG. Also, FTIR analysis of **L** (Fig. 1c) showed the almost complete disappearance of –OH group absorption of the starting PEG at 3317 cm<sup>–1</sup>, as well as the disappearance of the band around 3258 cm<sup>–1</sup>, which was ascribed to free N–H vibration mode in 2,2'-dipyriddyamine, confirmed clearly the linkage of dipyriddyamine with PEG chains. In addition, some additional absorption bands of **L** around 771 cm<sup>–1</sup> and in the region of 1400–1600 cm<sup>–1</sup> appeared, which was



**Fig. 1** FTIR spectra of (a) PEG-2000, (b) 2,2'-dipyriddyamine, (c) the functionalized PEG (**L**), (d) Pd(II)-**L** complex.

unambiguously attributed to the vibrations of pyridyl rings<sup>18</sup> in comparison with the absorption bands of PEG (Fig. 1a, 1b, 1c). The distinct changes of the hydrophilic ligand (**L**) before and after combination with palladium acetate in the FTIR spectra (around 1527 cm<sup>–1</sup>) strongly suggested the coordination of Pd(OAc)<sub>2</sub> with pyridyl rings (Fig. 1c and 1d). The UV/Vis spectra of the functionalized PEG (**L**) after coordination with Pd(OAc)<sub>2</sub> showed remarkable differences in the intensity and wavelength, which implied the occurrence of electron transfer between the pyridyl groups and Pd(OAc)<sub>2</sub>, in other words, the formation of the Pd(II) complex (Fig. 2a and 2d). Actually,



**Fig. 2** UV/Vis spectrum of (a) the functionalized PEG (**L**), (b) Pd(0) species obtained by reducing Pd(II)-**L** complex with H<sub>2</sub>, (c) Pd(0) species after styrene oxidation for 15 h, (d) Pd(II)-**L** complex, (e) Pd(II)-**L** complex after styrene oxidation for 15 h, (f) Pd(II)-**L** complex after 4 catalytic recycles.

**Table 1** Aerobic oxidation of styrene by using various catalysts in water<sup>a</sup>

Entry	T(°C)	t(h)	Con.(%)	Sel.(%)			
				Benzaldehyde	Acetophenone	Benzoic acid	Others
1	60	8	Trace	—	—	—	—
2 <sup>b</sup>	80	15	Trace	—	—	—	—
3	80	8	24.2	84.9	13.5	0	1.6
4	80	12	98.0	82.0	1.6	9.5	5.9
5 <sup>c</sup>	80	12	31.6	77.0	10.5	3.9	8.6
6 <sup>d</sup>	80	12	47.6	83.6	12.1	0	4.3
7 <sup>e</sup>	80	15	48.2	67.4	24.9	2.8	4.9
8 <sup>f</sup>	80	12	67.9	87.9	1.2	3.3	7.6

<sup>a</sup> Conditions: 8 ml of Pd(II)-L complex solution ([Pd] = 2.17 mmol/L), 1.75 mmol styrene, styrene/Pd = 100:1 (molar ratio), 0.5 MPa O<sub>2</sub>. <sup>b</sup> In the absence of any catalyst. <sup>c</sup> In the absence of L. <sup>d</sup> Pyridine as the ligand, pyridine/Pd = 4:1 (mole ratio). <sup>e</sup> With commercial Pd/C as catalyst. <sup>f</sup> Pd(0) species as catalyst obtained by reducing Pd(II)-L complex with H<sub>2</sub>.

the possible coordination mode of palladium(II)-dipyridylamine (1:1) complexes has been studied in detail.<sup>19</sup>

#### Aerobic oxidation of styrene catalyzed by water-soluble Pd complex in water

In our studies, the stable Pd(II)-L complex was successfully utilized for the effective oxidation of styrene using molecular oxygen as oxidant in aqueous phase. In the present system, styrene could be oxidized to benzaldehyde, acetophenone, benzoic acid and traces of other by-products, as shown in Table 1. In the absence of any catalyst, the aerobic oxidation of styrene did not take place at all (Table 1, entry 2). The reaction did not occur at 60 °C but proceeded at higher temperature (80 °C), (Table 1, entries 1 and 3). It was worth noting that the present water-soluble catalyst can be used under more mild conditions, compared with palladium(II) bathophenanthroline complex catalytic system which needed higher temperature (100 °C) and the addition of base (NaOAc).<sup>6b</sup> To our surprise, benzaldehyde was obtained as a main product with up to 82.0% selectivity (Table 1, entry 4), which was remarkably different from Wacker-type oxidation with ketones as the main products by using Pd(II) complex in water<sup>6b</sup> or Pd(II) species

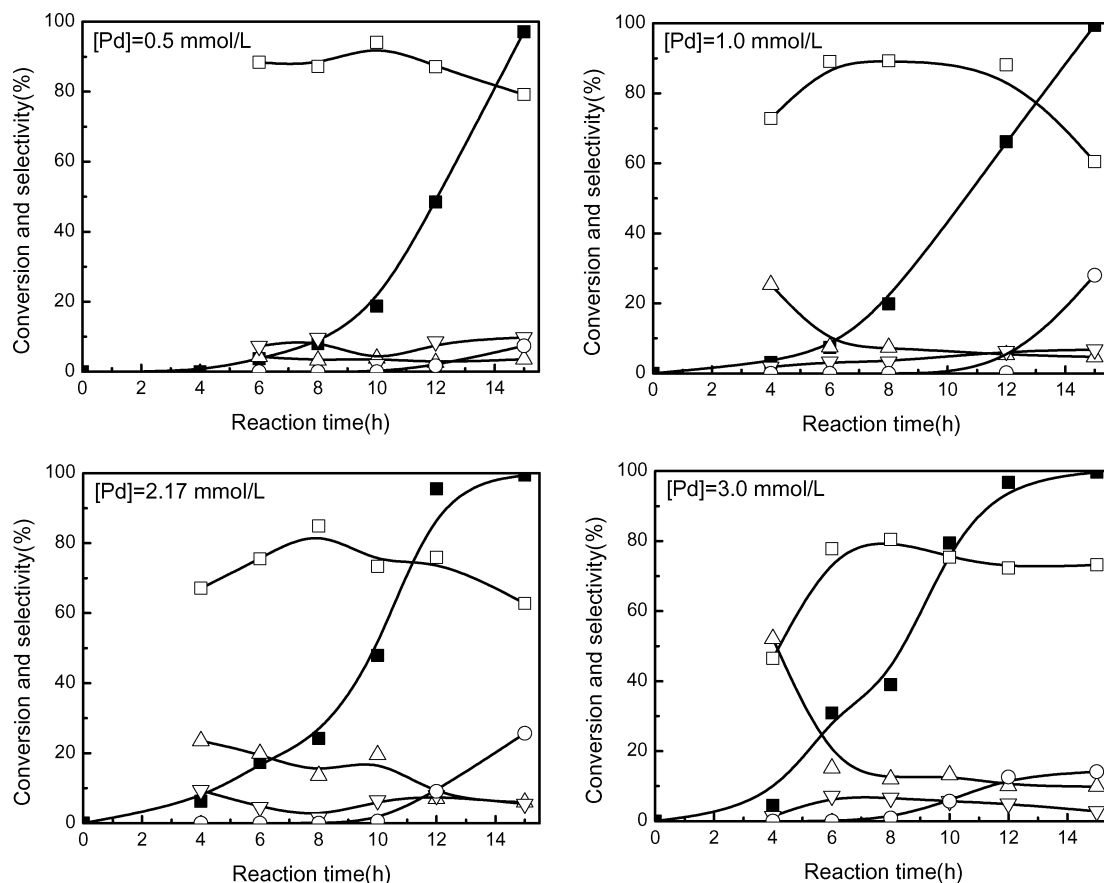
(PdCl<sub>2</sub> or Pd[(-)-sparteine]Cl<sub>2</sub>) in DMA/H<sub>2</sub>O solvent system.<sup>20</sup> The high selectivity to benzaldehyde by using present water-soluble catalyst is especially noteworthy because styrene is a notoriously difficult substrate due to facile polymerization and isomerization. To our best knowledge, this is the first example of the Pd(OAc)<sub>2</sub>-catalyzed aerobic oxidation of styrene to benzaldehyde in high selectivity in water. The various catalysts have also been examined for aerobic oxidation of styrene, and the results are summarized in Table 1. The lower conversion was obtained in the absence of L and the water-soluble monodentate ligand pyridine was proved to be much less effective (Table 1 entries 5, 6). The commercial Pd/C catalyst gave a poor conversion of 48.2% and a low benzaldehyde selectivity of 67.4% (Table 1 entry 7).

Experiments were also carried out to examine the recyclability of the present catalyst. After 8 times repeated catalytic oxidation of styrene, there was no loss of catalytic activity (Table 2 entries 1–8) and no obvious color change of the catalyst was visually observed. Further, this recovered catalyst solution was continuously employed for oxidation of the substituted styrenes. All the results showed relatively high conversions of the substituted styrenes under the same reaction conditions. The oxidation of 4-methylstyrene afforded the corresponding

**Table 2** Recyclable aerobic oxidation reaction of styrene with different substituting groups in water<sup>a</sup>

Entry	Substrates	Run	Con.(%)	Sel.(%)			
				Benzaldehyde	Acetophenone	Benzoic acid	Others
1	Styrene	1	98.0	82.0	1.6	9.5	5.9
2		2	99.3	78.8	1.4	15.7	4.1
3		3	99.2	80.3	0.8	14.2	4.7
4		4	96.9	81.7	1.1	10.7	6.5
5		5	96.5	85.9	0.5	8.0	5.6
6		6	95.4	86.3	0.7	6.6	6.4
7		7	98.9	81.4	0.3	12.8	5.5
8		8	96.4	78.4	0.6	15.6	5.4
9	4-Methylstyrene	9	99.5	4-Methyl-benzaldehyde	4'-Methyl-acetophenone	4-Methyl-benzoic acid	Others
10		10	99.4	14.8	1.0	80.3	3.9
11	4-Chlorostyrene	11	98.0	15.1	1.4	78.4	5.1
12		12	99.0	4-Chloro-benzaldehyde	4'-Chloro-acetophenone	4-Chloro-benzoic acid	Others
				28.6	5.8	63.4	2.2
				28.9	4.7	64.6	1.8

<sup>a</sup> Conditions: 8 ml of Pd(II)-L complex solution ([Pd] = 2.17 mmol/L), 1.75 mmol substrate, substrate/Pd = 100:1 (molar ratio), 80 °C, 12 h, 0.5 MPa O<sub>2</sub>.



**Fig. 3** The dependence of reaction time on styrene conversion and product selectivity at different [Pd]: (■) conversion of styrene, (□) selectivity to benzaldehyde, (○) selectivity to benzoic acid, (△) selectivity to acetophenone, (▽) selectivity to other by-products. Reaction conditions: 1.75 mmol styrene, 8 ml of catalyst solution, 80 °C, 0.5 MPa O<sub>2</sub>.

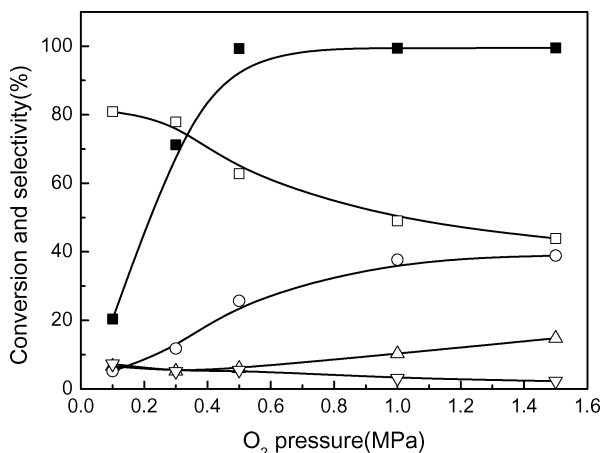
acid as a main product (Table 2 entries 9, 10), probably because the presence of the electron-donating group (–CH<sub>3</sub>) at the *para*-position of styrene increased the reactivity of styrene, while the electron-withdrawing group (–Cl) at the *para*-position of styrene decreased slightly the selectivity to the corresponding acid, but favored the formation of 4-chlorobenzaldehyde (Table 2 entries 11, 12). It was worth noting that the catalytic performance of the recovered catalyst for the oxidation of the substituted styrenes was similar to that of the fresh catalyst (results not shown). These results showed that this catalytic system was highly stable and could be recycled at least 12 times without loss of catalytic activity. The substituting groups in the aromatic rings of styrene affected the product selectivity significantly.

The time profile of the aerobic oxidation of styrene at different palladium concentration was monitored periodically under 80 °C and 0.5 MPa O<sub>2</sub>. As shown in Fig. 3, different [Pd] has some influences on the catalytic performance of styrene oxidation. An induction period of about 4 h was observed, which was presumed to form a catalytically active species. The reaction rate increased with [Pd] but the selectivity to benzaldehyde slightly decreased. As the reaction time was prolonged, the selectivity for benzaldehyde decreased slightly, and correspondingly, the selectivity to benzoic acid gradually increased, but the total selectivity to benzaldehyde and benzoic acid showed almost no change. These results implied that the trace amount of benzoic acid was formed by further reaction of benzaldehyde, and the

formation of benzaldehyde and acetophenone might proceed in parallel pathways.

The effect of O<sub>2</sub> pressure on styrene oxidation has also been examined. As shown in Fig. 4, O<sub>2</sub> pressure had a noticeable influence on the catalytic performance. With increasing O<sub>2</sub> pressure, the conversion of styrene was improved remarkably and the full conversion achieved at 0.5 MPa of molecular oxygen for 15 h, while the selectivity to benzaldehyde decreased due to the further oxidation to produce benzoic acid under higher O<sub>2</sub> pressure, and the selectivity to other products almost remained unchanged. This can be explained by the fact that the solubility of O<sub>2</sub> in water was improved with increasing O<sub>2</sub> pressure, and thus the mass transfer rate was enhanced;<sup>21</sup> in addition, increasing O<sub>2</sub> pressure could promote the formation of Pd(II) active species during reaction, which also led to the consequent increase of reaction rate.

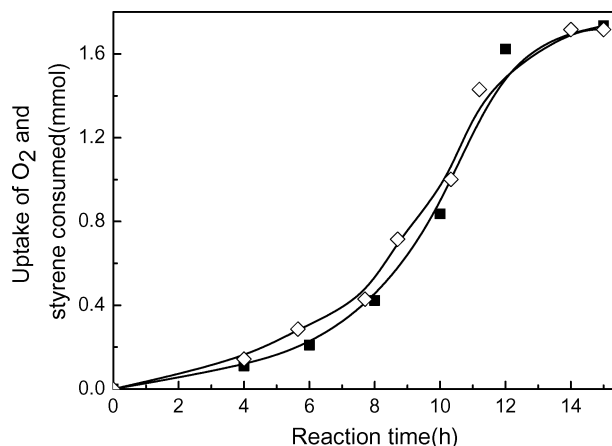
To probe the state of Pd complex during reaction, Pd(II)-L complex has been further examined during the reaction by using UV/Vis spectra. It was found that the absorption spectrums of Pd(II) complex were almost identical before and after reaction, and the complex maintained its geometry and electronic surrounding even after 4 runs (Fig. 2d, 2e, 2f). Additionally, under the same conditions, the absorption spectra of Pd(0) species was somewhat different from that of Pd(II) complex (Fig. 2b, 2d). It was very interesting that the absorption spectra of Pd(0) species after aerobic reaction was very similar to that of Pd(II),



**Fig. 4** The dependence of  $O_2$  pressure on styrene conversion and products selectivity: (■) conversion of styrene, (□) selectivity to benzaldehyde, (○) selectivity to benzoic acid, (△) selectivity to acetophenone, (▽) selectivity to other by-products. Reaction conditions: 1.75 mmol styrene, 8 ml of catalyst aqueous solution ( $[Pd] = 2.17$  mmol/L),  $80^\circ C$ , 15 h.

which indicated that Pd(0) can be easily converted to Pd(II) in the present conditions probably because of the decrease of the redox potential of Pd(II)/Pd(0) due to the presence of the bidentate nitrogen ligand.<sup>6c</sup> The above results indicated that Pd(II) complex might serve as the true catalytically active species in the present system, and this was the reason why Pd(0) species showed the lower catalytic activity for styrene oxidation (entry 8 in Table 1).

The relationship between  $O_2$  uptake and the amount of styrene consumed has also been investigated. As shown in Fig. 5,  $O_2$  uptake correlates well with the amount of styrene consumed. Interestingly, it was found that about 1 mol  $O_2$  was consumed for converting 1 mol styrene, which was different from the conventional Wacker-type mechanism where the molar ratio of olefin consumed to  $O_2$  uptake must be two theoretically.<sup>22</sup> Thus, a mechanism different from the Wacker-type should therefore be considered. Although the detailed reaction mechanism is not very clear at this stage, the plausible mechanism may be as follows (Fig. 6): in the first step, a Pd–H species was formed *via*  $\beta$ -H elimination of the Pd–olefin intermediate, followed by the insertion of  $O_2$  to give a Pd(II)–OOH species.<sup>23</sup> After that, a paladacycle was formed *via* insertion of the olefin into a Pd(II)–OOH species followed by an  $\alpha$ -hydride shift.<sup>24</sup> Then, a different decomposition path of the intermediate paladacycle may facilitate oxygen-atom transfer to C=C double bonds and homolytic bond cleavage, which has been used to account for the observed formation of oxidatively cleaved products in the aerobic oxidation of styrene.<sup>15,25</sup> This mechanism can explain the existence of an induction period during the reaction. Furthermore, more effective oxygenation of Pd–H bond to occur with increasing  $O_2$  pressure should enhance reaction rate, which was also in agreement with our observation. Experimentally, in the course of the Pd(II) complex-catalyzed oxidation of styrene into benzaldehyde, the by-product  $CO_2$ , possibly formed *via* the reoxidation of formaldehyde, was detected in gas phase by GC analysis.



**Fig. 5** Time profile of styrene oxidation: the relationship between  $O_2$  uptake (◇) and the amount of styrene consumed (■). Reaction conditions: 1.75 mmol styrene, 8 ml of catalyst aqueous solution ( $[Pd] = 2.17$  mmol/L),  $0.5$  MPa  $O_2$ ,  $80^\circ C$ .

## Conclusion

In summary, we have developed an environmentally benign water-soluble Pd(II) complex as a catalyst for the selective aerobic oxidation of styrene to benzaldehyde in high selectivity without any additives in the aqueous phase. The water-soluble Pd(II) complex was proved to be stable and highly catalytically active under the present conditions. In particular, the catalyst was easily recovered and could be reused at least twelve times without significant decrease in catalytic performance. Evaluating the process with a broader scope of substrates and further mechanism investigating are in progress in our laboratory.

## Experimental

### General remarks

PEG-2000 and sodium hydride (95%) were obtained from SCRC (Sinopharm Chemical Reagent Co, Ltd, Shanghai). 2,2'-Dipyridylamine and palladium acetate were purchased from Aldrich. All organic solvents used in this work were dried by standard procedures and the synthesis of catalyst materials was performed under nitrogen. All NMR spectra were recorded on a Bruker Avance 500 instrument (500 MHz  $^1H$ , 125 MHz  $^{13}C$ ) using  $CDCl_3$  and TMS as solvent and reference, respectively. Chemical shifts ( $\delta$ ) were given in parts per million and coupling constants ( $J$ ) in hertz. FTIR spectra were recorded at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna 550). The UV/Vis measurements were performed using a Varian Cary 500 spectrophotometer. The products were analyzed by GC and GC–MS equipped with a HP-5MS column (30 m long, 0.25 mm i.d., 0.25  $\mu m$  film thickness).

### Synthesis of the functionalized PEG (L)

PEG-2000 (10.0 g, 5 mmol) was dried under vacuum at  $60^\circ C$  for 2 h and then dissolved in anhyd- $CH_2Cl_2$  (40 mL). Triethylamine (2.02 g, 20 mmol) was added to the solution subsequently, and the mixture was cooled to  $0^\circ C$  with stirring. Then mesyl chloride



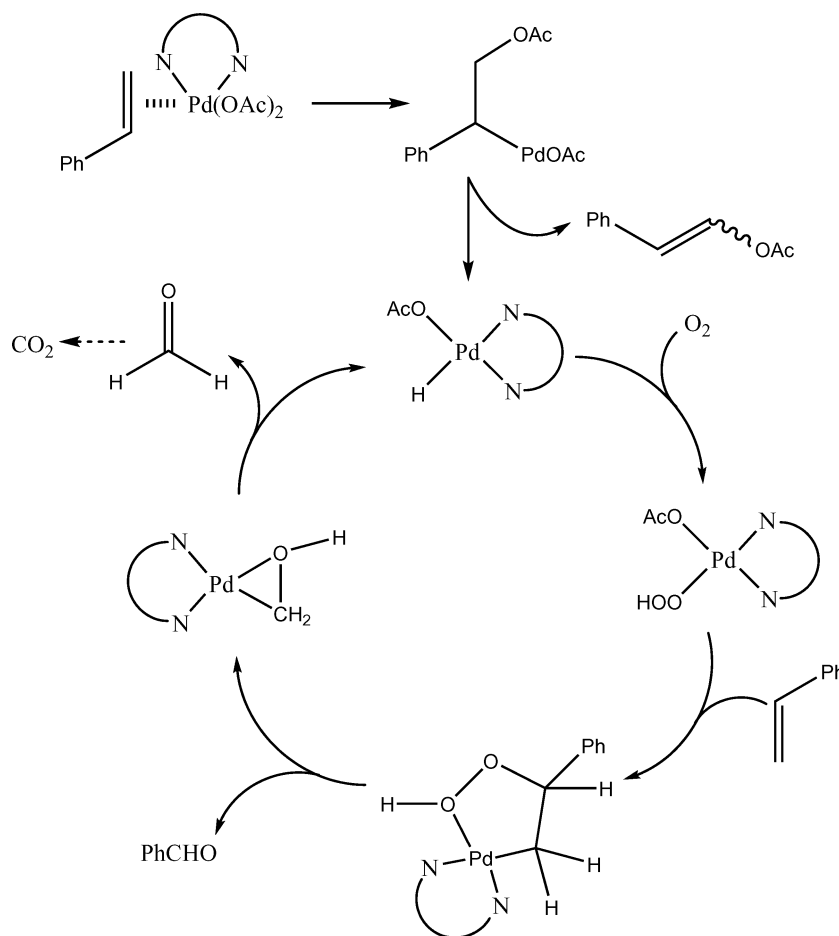


Fig. 6 The catalytic mechanism proposed for styrene oxidation with water-soluble Pd(II) complex.

(3.21 g, 28 mmol) was added slowly, and the mixture was stirred for 24 h at room temperature. The  $\text{CH}_2\text{Cl}_2$  was removed and then the residue was dispersed completely in toluene (25 mL), followed by filtration to remove insoluble triethylamine hydrochloride. The remaining filtrate was concentrated to one third of the solution volume and cooled to 0 °C, and then anhydr- $\text{Et}_2\text{O}$  (200 mL) was slowly added with stirring. After 1 h, a white solid (PEG dimesylate) was collected by filtration and washed with  $\text{Et}_2\text{O}$  three times.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 4.39 (t, 4 H), 3.50–3.73 (m, PEG), 3.09 (s, 6 H).

2,2'-Dipyridylamine (0.67 g, 3.91 mmol) was dissolved in anhydr-DMF (5 mL). To this solution was added NaH (0.1 g, 4.17 mmol), and the resulting mixture was stirred for 2 h at 50 °C, after which, PEG dimesylate (4.21 g, 1.95 mmol) dissolved in DMF (10 mL) was added. The solution was stirred at 90 °C for 4 h and then DMF was evaporated under reduced pressure. The brown residue was redissolved in benzene (15 mL) and filtered to remove residue. The volume of organic layer was reduced by 95% under reduced pressure. The remaining solution was cooled to 0 °C, and anhydr- $\text{Et}_2\text{O}$  (100 mL) was slowly added with stirring. Yellow solid (L) was obtained, then filtered and washed with  $\text{Et}_2\text{O}$  three times.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 8.25 (dt, 4H), 7.44 (m, 4H), 7.08 (dd, 4H), 6.79 (m, 4H), 4.32 (t, 4H), 3.48–3.70 (m, PEG).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 155.7, 148.4, 137.6, 117.6, 115.5, 70–72, 48.3.

#### Typical preparation procedure of water-soluble catalyst

The catalyst solution was prepared by stirring  $\text{Pd}(\text{OAc})_2$  (3.9 mg, 0.017 mmol) and L (22 mg, 0.0087 mmol) in water (8.0 mL) overnight at room temperature to give a clear yellow-orange solution. Pd(0) species were obtained by reducing Pd(II)-L complex with  $\text{H}_2$  at room temperature for 30 min, and the color of the solution changed from orange to black, which indicated the formation of the Pd(0) species.

#### Typical procedure for the aerobic oxidation of styrene in water

Standard catalytic experiments were carried out in a 50 mL autoclave. The autoclave was flushed with 0.5 MPa oxygen three times and cooled to 0 °C, charged with the catalyst solution (0.0175 mmol Pd complex in 8.0 mL water), styrene (1.75 mmol) and internal standard (n-heptane). Then the autoclave was pressurized with oxygen up to the required pressure and heated to 80 °C for an appropriate time. After reaction, the autoclave was cooled to 0 °C and released pressure slowly. Any volatile material was collected in a cold trap. The reaction mixture was extracted with  $\text{Et}_2\text{O}$  three times and the organic layer was dried over  $\text{MgSO}_4$  and analyzed by GC. Afterwards, the recovered aqueous solution was reused for the next run without any further procedure. The structures of the products were confirmed by mass spectral data and comparison with the literature. The

selectivity was calculated as molar percentage of the consumed styrene to a certain product per mol of reacted styrene.

### The experiment for O<sub>2</sub> uptake

The O<sub>2</sub> uptake experiment was carried out by following steps: The autoclave (50 ml) was first charged with the catalyst solution (0.0175 mmol Pd complex in 8.0 ml water), styrene (1.75 mmol) and internal standard (n-heptane), and then the autoclave was attached to O<sub>2</sub> storage vessel with known volume. Afterwards, the autoclave was pressurized with oxygen and heated to 80 °C (0.5 MPa) for 15 h. The decrease of pressure was monitored by a pressure transducer and recorded by using a computer. The recorded pressure values were converted following the ideal gas equation. A blank experiment was performed to measure the solubility of O<sub>2</sub> in catalyst solution in the absence of styrene for calibrating O<sub>2</sub> uptake in the oxidation reaction. In each parallel experiment, a sample was investigated using GC analysis to check conversion and selectivity at different reaction time.

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