



Short communication

# Effect of the types of stabilizers and size distribution on catalytic activity of palladium nanoparticles in the carboxylative coupling reaction

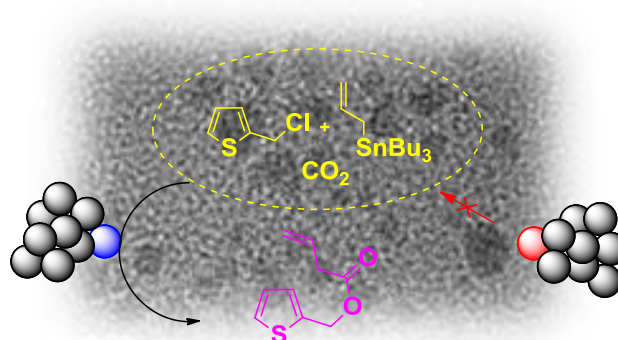
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## Abstract

Palladium nanoparticles (Pd NPs) generated in situ and stabilized by quaternary ammonium salts were used in three-component coupling reaction as the catalyst. Cations and anions of quaternary ammonium salts influenced the catalytic activity of Pd NPs, and tetrabutyl-ammonium bromide (TBAB) proved to be the best stabilizer. (2.23 ± 0.58) nm-sized Pd NPs showed the best catalytic activity under the molar ratio 1/30 [Pd(acac)<sub>2</sub>/TBAB]. The mercury poisoning test demonstrated the reaction occurred on the surface of Pd NPs. Pd NPs could be recycled for four times without significant loss in catalytic activity.

**Graphical abstract** The mercury poisoning tests demonstrated carboxylative coupling reaction occurred on the surface of Pd NPs which generated in situ, the types and additive amount of stabilizers influenced the catalytic activity of this catalytic system which could be recycled.



**Keywords** Stabilizer · Size distribution · Nanoparticles · Carboxylative coupling · CO<sub>2</sub> · Organic

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## 1 Introduction

Over the past few years, metal nanoparticles (MNPs) catalysts have attracted much interest and been widely used in many types of coupling reactions [1–3], such as Heck [4], Suzuki [5, 6], Sonogashira [7, 8], Stille [9, 10], Ullmann [11, 12], and Hiyama reactions [13, 14]. MNPs catalysts are usually better than the corresponding molecular catalysts on catalytic activity due to their large surface area, so, they need protective agents to avoid the formation of bulk metal. MNPs are generally stabilised by polymeric molecules [15, 16], tetraalkylammonium salts [17, 18], and ionic liquids [19, 20]. The first example of Heck coupling reactions under ligand-free conditions was successfully conducted by using Pd(OAc)<sub>2</sub>/<sup>n</sup>Bu<sub>4</sub>NCl as the catalyst and phase-transfer catalyst in 1984, however, no person realized that this catalytic system was promoted by Pd NPs at that time [21]. Recently, the carboxylative coupling reactions were successfully conducted by our group using Pd NPs in the presence of quaternary ammonium salts as the stabilizer, but the effect of quaternary ammonium salts and size distribution of Pd NPs on catalytic activity was not discussed [22].

Herein, we use the carboxylative coupling reaction of (2-chloromethyl)thiophene, allyltributylstannane, and carbon dioxide as the model reaction (Scheme 1), reveal the effect of the types of stabilizers and size distribution on catalytic activity of Pd NPs by transmission electron microscopy (TEM) studies, confirm whether the reaction occurred on the surface of Pd NPs, and explore the recyclability of this catalytic system.

## 2 Experimental

### 2.1 Catalytic activity measurement of Pd NPs stabilized by different types of quaternary ammonium salts

Pd(acac)<sub>2</sub> (7.6 mg, 0.025 mmol), quaternary ammonium salt (0.7 mmol), 2-(chloromethyl)-thiophene (66.0 mg, 0.5 mmol), allyltributylstannane (199.0 mg, 0.6 mmol), and THF (5 mL) were placed in a 50 mL autoclave with a magnetic stir bar under a N<sub>2</sub> atmosphere. The autoclave was purged with CO<sub>2</sub> three times, filled with CO<sub>2</sub> to 2 MPa

pressure, and heated to 70 °C for 24 h. The autoclave was allowed to cool to room temperature and the remaining CO<sub>2</sub> was vented. The resultant mixture was evaporated in vacuo to give the crude product, which was then purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:20) to afford benzyl but-3-enoate as a yellowish oil [22]. (TMAB: tetramethyl-ammonium bromide; TOAB: tetraoctyl-ammonium bromide; CTMAB: hexadecyl trimethyl ammonium bromide; TBAF: tetrabutyl-ammonium fluoride; TBAC: tetrabutyl-ammonium chloride; TBAI: tetrabutyl-ammonium iodide.) TEM was performed on a Tecnai G2 microscope operating at 120 kV. After the carboxylative coupling reaction of 2-(chloromethyl)-thiophene with allyltributylstannane was performed for 24 h under optimized reaction conditions, the resultant mixture was used for TEM determination.

### 2.2 Size distribution control and catalytic activity measurement of Pd NPs by variation of amount of TBAB

In the case of this reaction, we used TBAB in different molar ratio with respect to Pd(acac)<sub>2</sub> like 10:1, 20:1, 30:1, and 40:1 to see if it affected the size of Pd NPs, the reaction was conducted using the same procedure described above. The gradual variation in size of nanoparticles with different molar ratio is revealed clearly in the TEM studies.

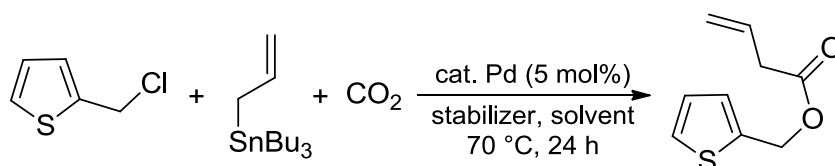
### 2.3 Hg (0) poisoning test

As above procedure, a reaction of 2-(chloromethyl)-thiophene (66.0 mg, 0.5 mmol), allyltributylstannane (199.0 mg, 0.6 mmol), Pd(acac)<sub>2</sub> (7.6 mg, 0.025 mmol), quaternary ammonium salt (0.7 mmol), THF (5 mL), with the addition of elemental mercury (2.5 mmol, 100 equiv, 501.5 mg) (relative to palladium), and were placed in a 50 mL autoclave with a magnetic stir bar under a N<sub>2</sub> atmosphere. The autoclave was purged with CO<sub>2</sub> three times, filled with CO<sub>2</sub> to 2 MPa pressure, and heated to 70 °C for 24 h [23].

### 2.4 Recycling experiment

After reaction completion, the mixture was then extracted with *n*-hexane (3 × 5 mL). The top layer was collected and purified via silica gel chromatography. The Pd NPs (under

**Scheme 1** Pd NPs-catalyzed carboxylative coupling reaction



layer) was subjected to another run by charging it with the same substrates as mentioned above without further addition of Pd(acac)<sub>2</sub> and TBAB.

### 3 Result and discussion

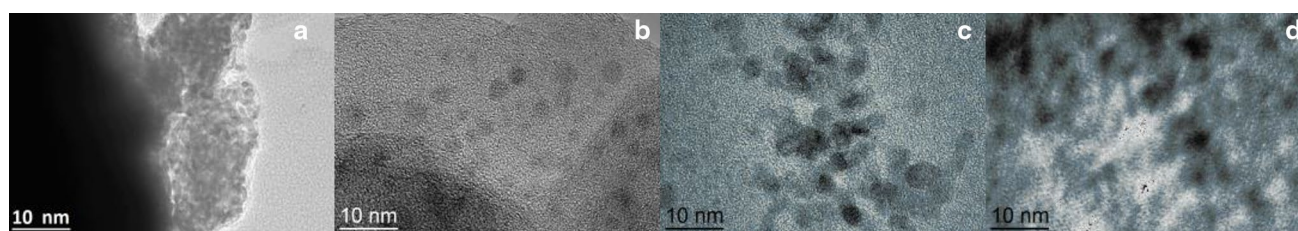
The TEM studies of Pd NPs by using quaternary ammonium salts as the stabilizer with different cations are shown in Fig. 1. It is seen that the serious conglomeration when used TMAB or CTMAB as the stabilizer, and the yield of the product is 0 or 20%, respectively. On the other hand, the uniform distribution and good dispersibility of Pd NPs are observed when the TBAB added with the 73% yield of the product. Although the dispersed nanoparticles are seen when TOAB as the stabilizer, conglomeration can not be prevented with the 57% yield of the product. The results indicated that the quaternary ammonium salts with longer or shorter alkyl chains in cations are not conducive to the dispersion of Pd NPs, and higher catalytic activity is revealed when TBAB is added which including <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup>.

Figure 2 shows the TEM studies of Pd NPs by using quaternary ammonium salts as the stabilizer with different anions. The Pd NPs are serious coated by TBAF, TBAC or TBAI, this phenomenon leads to the decrease of its catalytic activity, and the yield of the product is 13%, 25% or 17%, respectively. Better catalytic activity and uniform dispersion are observed when using TBAB as the stabilizer.

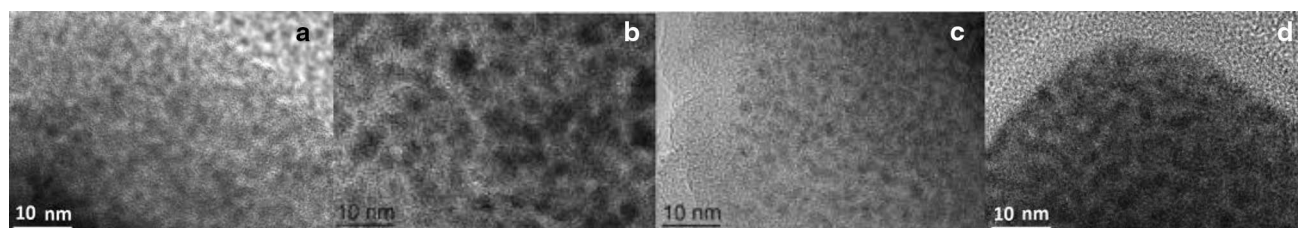
The effect of stabilizer on the catalytic activity of Pd NPs, not only because of the types of stabilizers, but also due

to the size of Pd NPs. TEM studies of Pd NPs with varying Pd/TBAB molar ratio and their corresponding size distribution images were shown in Fig. 3. Size distribution of Pd NPs were  $3.56 \pm 0.77$  nm and  $3.37 \pm 0.60$  nm when Pd/TBAB molar ratio 1/10 and 1/20 were used. At this moment, larger particle size and lower catalytic activity were observed with the 7% and 41% yields of the product, and serious conglomeration were revealed. Pd NPs with more average and smaller diameter of  $2.23 \pm 0.58$  nm were generated when Pd/TBAB molar ratio 1/30 was used, the best catalytic activity and yield (73%) were achieved in this case. However, continued to increase the molar ratio to 1/40, no significant loss in catalytic activity (70% yield) with the diameter of  $2.50 \pm 0.48$  nm.

Based on the TEM studies, a plausible growth mechanism for Pd NPs was speculated. Pd-rich and Pd-poor phases were formed with the increase of Pd/TBAB molar ratio, then nucleation of amorphous nanoclusters within the Pd-rich phase, followed by crystallization of these amorphous clusters to formed Pd NPs with an ionic coating [24]. Although the Pd NPs showed good catalytic activity which generated in situ, the catalysis which occurred on the Pd NPs surface or by leached Pd species was still needed to assess. A large excess of Hg(0) was added to the model reaction under the standard conditions and no product was observed when the reaction finished. The Hg(0) poisoning experiments suggested that the reaction occurred on the Pd NPs surface and the active catalyst was very likely to be heterogeneous in nature. From the above, the nature of this catalytic system was not like a

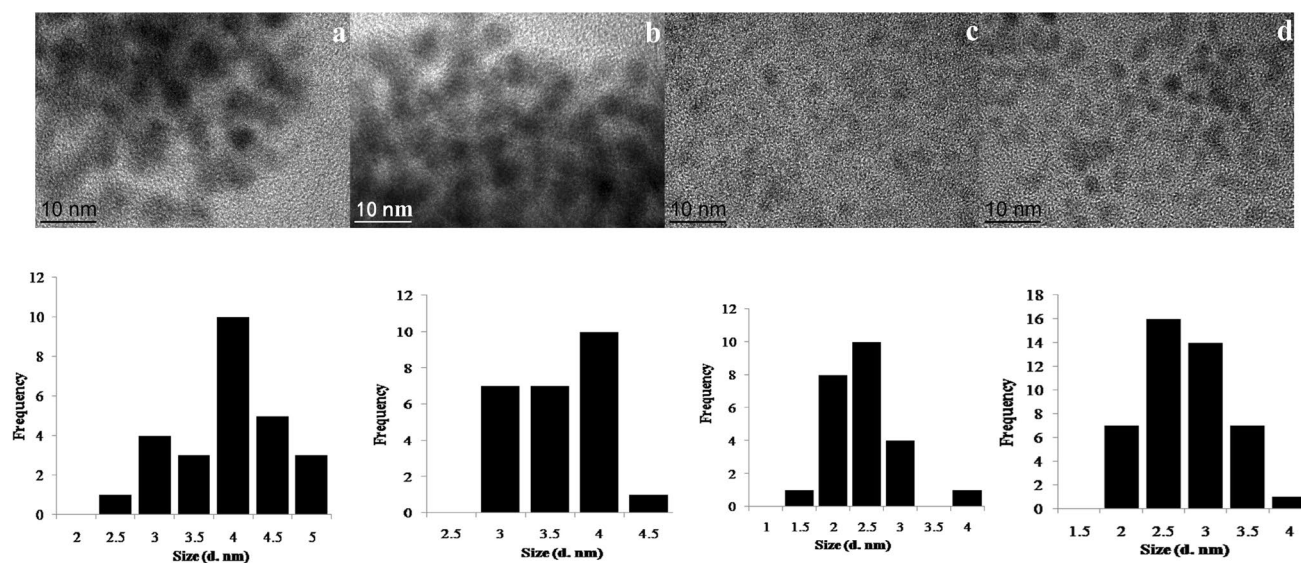


**Fig. 1** TEM studies of palladium nanoparticles by using quaternary ammonium salts as the stabilizer with different cations: **a** TMAB, **b** TBAB, **c** TOAB, and **d** CTMAB



**Fig. 2** TEM studies of palladium nanoparticles stabilized by quaternary ammonium salts containing different anions: **a** TBAF, **b** TBAC, **c** TBAB, **d** TBAI





**Fig. 3** TEM studies (up) of palladium nanoparticles with varying Pd/TBAB molar ratio and their corresponding size distribution images (down): **a** 1/10, **b** 1/20, **c** 1/30, **d** 1/40

Cocktail-type system, because no leaching for Pd and only Pd NPs were formed with an ionic coating in the catalytic system [25].

Studies were also conducted to assess the potential for recycling of the reaction medium. The trend of aggregation was observed after the two run recycling uses of Pd NPs, but without significant loss in catalytic activity. Pd black was found after four running four times, which led to a loss of the catalytic activity and the yield of product from 73% decrease to 54%.

## 4 Conclusion

In summary, we have successfully illustrated that the effects of types of stabilizers and size distribution of Pd NPs on the catalytic activity in the carboxylative coupling reaction of (2-chloromethyl)thiophene, allyltributylstannane, and carbon dioxide. Excellent catalytic activity was observed using TBAB as the stabilizer with an average and smaller diameter of  $2.23 \pm 0.58$  nm under Pd/TBAB molar ratio 1/30. The Hg (0) poisoning experiment suggested that the active catalyst was very likely to be heterogeneous in nature. Notably, this catalytic system generated in situ and could be recyclable. Further studies focusing on the reactions using magnetic Pd NPs as the catalyst are currently ongoing.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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