

## An efficient Approach to Modify the Catalyst Activity for the Hydrogenation of Nitrobenzene

Wei Min MO<sup>2</sup>, Bo Shun WAN<sup>1\*</sup>, Shi Jian LIAO<sup>1</sup>

<sup>1</sup>Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023

<sup>2</sup>College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014

**Abstract:** The addition of a suitable amount of PPh<sub>3</sub> to PdCl<sub>2</sub> or PdCl<sub>2</sub>(PhCN)<sub>2</sub> *in situ* can considerably increase the catalytic activity in the hydrogenation of nitrobenzene, while the catalytic activities of PdCl<sub>2</sub> (reduced)+PPh<sub>3</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> are very poor. The poisoning of catalyst by mercury indicates that the catalytically active species are composed of Pd(0) colloidal particles. Transmission electron micrographs show that the size of nanometric Pd(0) particles of PdCl<sub>2</sub> with PPh<sub>3</sub> added *in situ* is smaller than that of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or PdCl<sub>2</sub> (reduced)+PPh<sub>3</sub>. A synergic effect of bimetallic catalysts such as PdCl<sub>2</sub>+nPPh<sub>3</sub>+NiCl<sub>2</sub> (n= 0.5, 1) and PdCl<sub>2</sub>(PhCN)<sub>2</sub>+PPh<sub>3</sub>+FeCl<sub>3</sub> gives rise to a further increase in the catalytic activity.

**Keywords:** Bimetallic catalyst, synergic effect, catalytic hydrogenation, palladium.

Transition metal complexes have been used extensively for the hydrogenation in homogeneous system probably due to their high catalytic selectivities under mild operating conditions. In order to improve the homogeneous catalyst system, some studies on the homogeneous or soluble polymer-supported bimetallic catalysts have been recently carried out and enhanced activity, better selectivity were observed in selective hydrogenation, hydrodehalogenation, carbonylation, hydroformylation and regioselective hydroesterification<sup>1-6</sup>. The enhanced activity and better selectivity are due to the cooperative or successive participation of two metals. In this paper, we report that the addition of a suitable amount of PPh<sub>3</sub> to PdCl<sub>2</sub> or PdCl<sub>2</sub>(PhCN)<sub>2</sub>+PPh<sub>3</sub> *in situ* and a synergic effect of bimetallic catalysts such as PdCl<sub>2</sub>+nPPh<sub>3</sub>+NiCl<sub>2</sub> (n=0.5, 1) and PdCl<sub>2</sub>(PhCN)<sub>2</sub>+PPh<sub>3</sub>+FeCl<sub>3</sub> can greatly increase the catalytic activity for the hydrogenation of nitrobenzene to aniline. Our aim is to provide an easy and efficient approach to increase the catalyst activity further.

**Table 1** summarizes the results of three kinds of Pd catalysts for the hydrogenation of nitrobenzene at 60 °C in the presence of a base (NaOAc) under atmospheric pressure. The first kind of catalysts such as PdCl<sub>2</sub>(PPh<sub>3</sub>), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> exhibits very low catalytic activity (entries 1-3). The second kind of catalyst PdCl<sub>2</sub> (reduced)+PPh<sub>3</sub> (entry 4), obtained by treating PdCl<sub>2</sub> with H<sub>2</sub> and then adding PPh<sub>3</sub>, provides only 6% yield which is even lower than that of the reaction catalyzed by PdCl<sub>2</sub> itself (22%) (entry 5). The third kind of catalyst PdCl<sub>2</sub>+PPh<sub>3</sub> (entry 7), prepared by adding a suitable amount of PPh<sub>3</sub> to PdCl<sub>2</sub> *in situ*, gives high yield and the yield is related to the mole ratio

\* E-mail: bswan@dicp.ac.cn

of PPh<sub>3</sub>/Pd. The best result with 95% yield is obtained when the mole ratio of PPh<sub>3</sub> to Pd is 1, while the catalyst almost loses its activity entirely at a PPh<sub>3</sub>/Pd mole ratio equals 3 (entries 6-9). Likewise, it can be seen from **Table 1** that introducing a suitable amount of PPh<sub>3</sub> to PdCl<sub>2</sub>(PhCN)<sub>2</sub> *in situ* can also greatly enhance the catalytic activity in the hydrogenation of nitrobenzene (entries 10, 11). Based on the above results, it is apparent that in this case, the method of preparation of a catalyst with the same chemical composition plays an important role with respect to its catalytic behavior.

**Table 1** Catalytic hydrogenation of nitrobenzene<sup>a</sup>

entry	catalyst precursor	yield of aniline (%)
1	PdCl <sub>2</sub> (PPh <sub>3</sub> )	8
2	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	6
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	3
4	PdCl <sub>2</sub> (reduced)+PPh <sub>3</sub> <sup>b</sup>	6
5	PdCl <sub>2</sub>	22
6	PdCl <sub>2</sub> +0.5PPh <sub>3</sub>	54
7	PdCl <sub>2</sub> +PPh <sub>3</sub>	95
8	PdCl <sub>2</sub> +2PPh <sub>3</sub>	86
9	PdCl <sub>2</sub> +3PPh <sub>3</sub>	1
10	PdCl <sub>2</sub> (PhCN) <sub>2</sub>	10
11	PdCl <sub>2</sub> (PhCN) <sub>2</sub> +PPh <sub>3</sub>	74

<sup>a</sup> Conditions: catalyst,  $4 \times 10^{-3}$  mmol Pd; methanol, 15 mL; nitrobenzene, 4 mmol; NaOAc.3H<sub>2</sub>O, 4 mmol; H<sub>2</sub> 0.1 MPa, 60°C, 200 min. <sup>b</sup> After Pd catalyst was treated under H<sub>2</sub> for 10 min, PPh<sub>3</sub> and nitrobenzene were added successively. Other conditions were the same as (a).

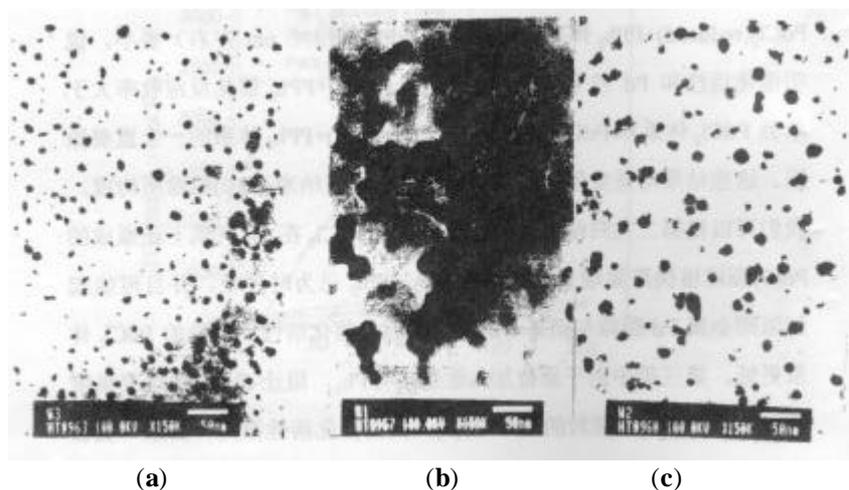
It has been reported that the colloidal Pd(0) particles are easily resulted from Pd complexes under H<sub>2</sub> atmosphere<sup>7</sup> and mercury can be used as a selective poison for the metallic colloidal catalysts, while the homogeneous catalysts (molecular active species) are unaffected<sup>8,9</sup>. We found that in the presence of excess Hg, all of the catalysts lost their activities entirely. This result suggested that the catalytically active species are composed of colloidal Pd(0) particles. Thus, transmission electron micrographs were taken for the PdCl<sub>2</sub>(PPh<sub>3</sub>), PdCl<sub>2</sub> (reduced)+PPh<sub>3</sub>, and PdCl<sub>2</sub>+PPh<sub>3</sub> catalysts after being exposed under H<sub>2</sub> (**Figure 1**). The transmission electron micrographs show that Pd particles of nanometric size are formed. The size of nanometric Pd(0) particles of PdCl<sub>2</sub> with PPh<sub>3</sub> added *in situ* (a) is smaller than that of PdCl<sub>2</sub>(PPh<sub>3</sub>) (b) or PdCl<sub>2</sub> (reduced)+PPh<sub>3</sub> (c). Obviously, the size of Pd(0) particles is one of the factors which influence the Pd catalyst activity.

**Table 2** Bimetallic catalysts for the hydrogenation of nitrobenzene

entry	catalyst precursor	yield of aniline (%)
12	PdCl <sub>2</sub> +0.5PPh <sub>3</sub> +NiCl <sub>2</sub>	83
13	PdCl <sub>2</sub> +PPh <sub>3</sub> +NiCl <sub>2</sub>	99
14	PdCl <sub>2</sub> +PPh <sub>3</sub> +Co(OAc) <sub>2</sub>	95
15	PdCl <sub>2</sub> (PhCN) <sub>2</sub> +PPh <sub>3</sub> +NiCl <sub>2</sub>	84
16	PdCl <sub>2</sub> (PhCN) <sub>2</sub> +PPh <sub>3</sub> +FeCl <sub>3</sub>	92

Reaction conditions were the same as in **Table 1** (a).

**Figure 1** Transmission electron micrographs of Pd particles resulted from PdCl<sub>2</sub>+PPh<sub>3</sub> (a), PdCl<sub>2</sub>(PPh<sub>3</sub>) (b) and PdCl<sub>2</sub>(reduced)+PPh<sub>3</sub> (c)



In order to improve the catalyst performance further, the bimetallic catalysts were prepared by adding a second metal component which exhibits no catalytic activity such as NiCl<sub>2</sub>, FeCl<sub>3</sub> and Co(OAc)<sub>2</sub> as a modifier to PdCl<sub>2</sub>+nPPH<sub>3</sub> (n=0.5, 1) or PdCl<sub>2</sub>(PhCN)<sub>2</sub>+PPh<sub>3</sub> *in situ* and the results are listed in **Table 2**. It can be seen from **Table 1** and **2** that in most cases, the bimetallic catalysts enhance the catalytic activity. A bimetallic synergic effect is obvious. For example, PdCl<sub>2</sub>+nPPH<sub>3</sub>+NiCl<sub>2</sub> (n=0.5, 1) and PdCl<sub>2</sub>(PdCN)<sub>2</sub>+PPh<sub>3</sub>+FeCl<sub>3</sub> afford 83%, 99%, and 92% yield (entries 12, 13 and 16), respectively, which is higher than that of the corresponding monometallic Pd catalysts (entries 7 and 11). However, introducing Co(OAc)<sub>2</sub> to PdCl<sub>2</sub>+PPh<sub>3</sub> *in situ* does not exert influence on the reaction (entries 7 and 14). It shows that the addition of a suitable second transition metal compound to Pd catalyst can give rise to an obvious increase in the catalytic activity. It provides an easy and efficient approach to modify catalyst performance further.

### Acknowledgments

We thank the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for the financial support of this research.

### References

1. C. Q. Liu, Y. Xu, S. J. Liao, D. R. Yu, *J. Mol. Catal. A*, **2000**, *157*, 253.
2. Y. Gao, F. D. Wang, S. J. Liao, D. R. Yu, N. Sun, *React. Funct. Polym.*, **2000**, *44*, 65.
3. B. S. Wan, S. J. Liao, Y. Xu, D. R. Yu, *J. Mol. Catal. A*, **1998**, *136*, 263.
4. B. S. Wan, S. J. Liao, D. R. Yu, *React. Funct. Polym.*, **2000**, *45*, 55.
5. B. S. Wan, S. J. Liao, D. R. Yu, *Appl. Catal. A*, **1999**, *183*, 81.

6. H. Jiang, Y. Xu, S. J. Liao, D. R. Yu, H. Chen, X. J. Li, *J. Mol. Catal. A*, **1999**, *142*, 147.
7. G. Schmid, *Chem.Rev.*, **1992**, *92*, 1709.
8. D. R. Anton, R. H. Crabtree, *Organometallics*, **1983**, *2*, 855.
9. L. N. Lewis, N. Lewis, *J. Am. Chem. Soc.*, **1986**, *108*, 7228.

Received 19 February, 2001