Direct synthesis of Pd incorporated in mesoporous silica for solvent-free selective hydrogenation of chloronitrobenzenes

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HIGHLIGHTS

- Pd incorporated in mesoporous silica (Pd-MS) catalysts were prepared via direct synthesis method.
- The formation mechanism of Pd-MS catalysts with 1, 3, 5-trimethylbenzene (TMB) was proposed.
- The catalytic activity of Pd-MS-*x*-TMB increased with increasing pH value (*x* meant *x*/10 mL NH$_3$·H$_2$O).
- The selectivity to *p*-CAN was 99.9% at 100% *p*-CNB conversion by Pd-MS-50-TMB at 85 °C, 3.45 MPa and 2 h.
- Pd-MS-50-TMB was also found to be effective for solvent-free hydrogenation of *m*-CNB and *o*-CNB.

GRAPHICAL ABSTRACT
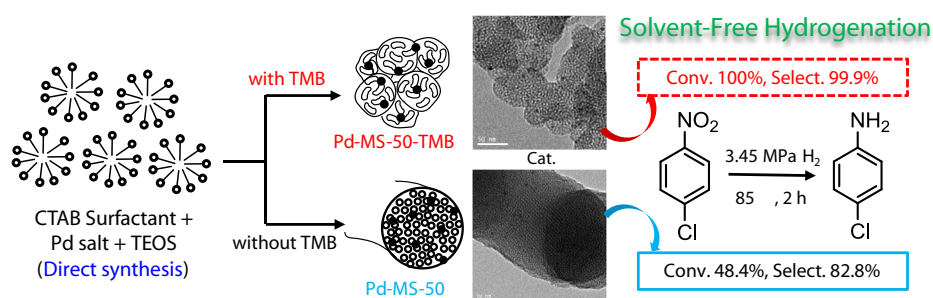
ABSTRACT

Pd incorporated in mesoporous silica (Pd-MS) catalysts were prepared by a direct synthesis method in the presence of 1, 3, 5-trimethylbenzene (TMB) and their formation mechanism was proposed. TMB not only acted as an effective expanding agent to enlarge pore size and pore volume of MS but also acted as a structure-directing agent to induce the formation of worm-like morphology. For solvent-free hydrogenation of *p*-chloronitrobenzene (*p*-CNB), a complete conversion of *p*-CNB with a selectivity towards *p*-chloroaniline of 99.9% over the Pd-MS catalyst with addition of TMB (Pd-MS-50-TMB, where 50 represented the addition of 5 mL of aqueous NH$_3$) was obtained at 85 °C and 3.45 MPa of H$_2$ in 2 h, while only 48.4% *p*-CNB conversion over Pd-MS-50 synthesized without TMB was obtained. The enhanced activity of the Pd-MS-50-TMB was not only attributed to the smaller size of Pd particles, but also to the worm-like morphology of the support with larger pore size and pore volume that could enhance mass transfer and allow the reactants more facile access to Pd for reaction.

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1. Introduction

Chloroanilines (CANs) are valuable organic intermediates that have been widely used in synthesizing polyesters, pesticides, herbicides, pharmaceuticals and dyes. They are generally synthesized via hydrogenation of chloronitrobenzene (CNBs) [1–5]. In the past

decades, various supported metal catalysts were described for liquid-phase hydrogenation of CNBs (*p*-CNB [6–9], *m*-CNB [3,4,10], and *o*-CNB [5,11–14]). However, the use of organic solvents as reaction medium in these hydrogenation reactions limits their practical use because it causes environmental waste and high-energy consumption for the subsequent separation of the reaction mixtures [12,15]. Reduction, elimination and prevention of hazardous substances and waste during hydrogenation reactions have received considerable attention in recent years because of

their reduced environmental impact and energy savings [16–18]. Thus, many supported metal catalysts systems have been proposed for synthesis of CANs via hydrogenation of CNBs under solvent-free conditions [19–21]. Sun et al. [19] used Pt-CeO$_2$ catalyst for solvent-free hydrogenation of o-CNB. A 99.0% o-CNB conversion with a selectivity of 99.2% towards o-CAN was obtained at 60 °C and a H$_2$ pressure of 3.0 MPa. Lian et al. [20] used Pt/Fe$_3$O$_4$ catalyst for solvent-free hydrogenation of o-CNB and m-CNB, resulting in a complete conversion of o-CNB and m-CNB at 60 °C and a H$_2$ pressure of 2.0 MPa. Fan et al. [21] developed a Pt/MWCNTs-Fe$_3$O$_4$ catalyst system for solvent-free hydrogenation of o-CNB and m-CNB and 99.0% o-CAN and 99.0% m-CAN yield were obtained at 60 °C and a H$_2$ pressure of 4.0 MPa in 1.5 h and 3 h, respectively.

However, the synthesis of the high production volume compound p-CAN via hydrogenation of p-CNB is still carried out in organic solvents over metal catalysts [3,6,8], partly due to the lack of effective and highly selective catalysts for synthesis in the absence of solvent. Moreover, for hydrogenation of p-CNB in organic solvent over common metal catalysts, it is difficult to completely avoid the hydrodechlorination of p-CAN to aniline (AN), especially at complete conversion of p-CNB [3,6,7], which limit its selectivity to the p-CAN. Hydrogenation of p-CNB at high temperatures such as 500 °C over Pt/TiO$_2$ catalyst [22] and 180 °C over Au/TiO$_2$ catalyst [7] were reported to achieve selectivity higher than 99.3% towards p-CAN with p-CNB conversion higher than 98%. In addition, hydrogenation of p-CNB in supercritical CO$_2$ (scCO$_2$) has also been applied to suppress the hydrodechlorination process [23]. However, the high energy consumption for hydrogenation at high temperatures and expensive equipment for hydrogenation in scCO$_2$ would limit the application of these processes at a large scale. For the highly effective production of p-CAN with reduced energy consumption, cost and environmental impact, the development of highly effective and selective catalysts for solvent-free hydrogenation of p-CNB is an essential challenge.

Pd NPs incorporated in support (typically porous silica) have been used widely as catalysts in chemical processes such as hydrogenation [24–28], CO oxidation [29–33] and C–C coupling reactions [34–38]. Generally, the incorporation of metal NPs within silica supports can be achieved by a post-synthetic deposition method and a direct synthesis method. However, the particle size and the dispersion of metal nanoparticles (NPs) of the supported metal catalysts prepared by the post-synthetic deposition method are difficult to control during the preparation processes, however, these two factors have great effects on the catalytic activity and selectivity [6,22,39]. Compared with the post-synthetic deposition method, the direct synthesis method that incorporates metal NPs or metal precursors in situ within the internal structure of silica support is simple and can yield a uniform distribution of confined NPs [40], and thus it has attracted more recent attention [40–42]. Many Pd-based catalysts have been successfully synthesized by direct synthesis with small Pd NPs stabilized and finely dispersed in the walls of nanostructured silica materials such as Pd/MCM-41 [43,44], Pd/SBA-15 nanocomposites [45,46], and Pd/SiO$_2$ [26]. Besides, the role of the support structure in modifying catalytic properties has also been recognized. On the one hand, pore size and morphology of the silica support may help optimize catalytic performance by improving inter-channel diffusion of reactants to catalytic sites and the desorption of products [47]. Thus, research has been focused on enlargement of mesopore size, allowing not only reactant reactants but also products to diffuse rapidly in the pores. On the other hand, the metal-support interactions have great impact on the electronic state and/or the morphology of metal nanoparticles, thus modifying nanoparticle and catalytic properties [6,48]. Thus, in recent years, great effort has focused on the direct synthesis of supported metal catalysts with introduction of stabilizing agents [36,49–51] that could provide appropriate interactions between the metal NPs and silica precursor during the formation of the MS and structure-directing agents [52] that influence the formation of micelles that lead to porous materials with special nanostructures in the formation process. Budroni et al. [36] used a mixture of 1-dodecanethiol and 3-mercaptopropyl trimethoxysilane to stabilize Pd NPs in a silica support by providing the organic links between the metal particles and inorganic sponge-like silica. Martinez et al. [50] used 4-dimethylaminopyridine and 3-mercaptopropyltriethoxysilane as capping agents to functionalize pre-synthesized Pd colloids in an organic phase and then transferred the organic solution to an aqueous phase for in situ incorporation with silica precursors. Linares et al. [51] used Triton X-100 as a structure-directing agent during the synthesis of different functional mesoporous silica materials by co-condensation of tetraethyl orthosilicate (TEOS) with three Pd(II) complexes containing trialkoxysilane terminal groups. TMB is reported to be a very effective in tailoring pore size and morphology of pristine MS support in post-synthetic deposition method [53,54]. However, to the best of our knowledge, neither the effect of TMB on the structure of metal incorporated MS catalysts synthesized by direct synthesis method nor the catalytic performances for the catalysts synthesized by direct synthesis method in the presence of TMB for solvent-free hydrogenation of CNBs has been reported.

Herein, a novel strategy to incorporate Pd NPs in situ within the internal structure of MS in the presence of TMB has been proposed. The Pd-MS catalysts with and without TMB were synthesized by direct synthesis method under basic conditions. The effect of TMB on the structure of catalysts was discussed and a possible formation mechanism of the catalysts synthesized by direct synthesis method in the presence of TMB was proposed. The catalytic performance of these catalysts for hydrogenation of p-CNB under solvent-free condition was further studied. An effective Pd-MS catalyst with addition of TMB for the solvent-free selective hydrogenation of p-CNB was synthesized by direct synthesis method in this study. Moreover, the solvent-free hydrogenation of the two other isomers (m-CNB and o-CNB) were also investigated.

2. Experimental

2.1. Catalyst preparation

2.1.1. Direct synthesis of Pd incorporated in MS (Pd-MS)

In a typical trial for synthesizing Pd-MS in the presence of TMB, cetyl trimethylammonium bromide (CTAB) (≥99.0%, Sigma-Aldrich, 2 g) and TMB (98%, Alfa-Aesar, 2 g) were dissolved in deionized water (100 mL) and stirred for 30 min. An aqueous solution (20 mL) of palladium nitrate dihydrate (Pd(NO$_3$)$_2$·2H$_2$O, Sigma-Aldrich, 75 mg) was added dropwise into the CTAB aqueous solution with TMB (ca. 1 wt% metal loading in silica). Next, TEOS (≥99.0%, Sigma-Aldrich, 10 mL) was added dropwise. Various quantities (0.5, 1, 3, and 5 mL) of 28% aqueous NH$_3$ (J. T. Baker) were subsequently added. Both the pH values of each gel mixture before (initial pH) and after (final pH) its hydrolysis-condensation reaction (40 °C, 12 h) were measured. The as-synthesized precipitates were filtered and washed with deionized water and anhydrous ethanol (≥99.8%, Sigma-Aldrich). The obtained products were dried at 80 °C overnight. The powders were calcined at 550 °C for 5 h in air flow and then reduced under a flow of H$_2$ (20 mL/min) at 400 °C for 4 h. The resulting gray powders were denoted as Pd-MS-x-TMB, where an x of 05, 10, 30, and 50 represented the addition of 0.5, 1, 3, and 5 mL of aqueous NH$_3$, respectively. For the synthesis of Pd-MS-x, an aqueous solution of Pd (NO$_3$)$_2$ was added into the CTAB aqueous solution without the