

# Transfer hydrogenation of nitrobenzene to aniline in neat water using Pd nanoparticles immobilized on amine-functionalized UiO-66

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Conventionally, preparation of amines relies on the homogeneous hydrogenation of nitro-compounds in the presence of a solvent and/or activation ligand. Heterogeneous production methods have also been developed, and the search for a facile and ecofriendly procedure that avoids the use of toxic solvents and high pressure hydrogen gas has gained particular interest. Catalytic transfer hydrogenation (CTH), by employing hydrogen donors such as formic acid (FA) is operationally simple and can avoid the use of molecular hydrogen gas. Metal-organic frameworks (MOFs) are emerging as important functional materials for gas storage, separation and catalysis owing to their high surface area, porosity and diverse functionalization available [2]. Herein, we report the synthesis of well dispersed Pd NPs on amine-functionalized UiO-66 (NH<sub>2</sub>-UiO-66) for CTH of nitrobenzene (NB) to aniline (AN) using FA in water medium under mild conditions.

NH<sub>2</sub>-UiO-66 was synthesized according to the solvothermal synthesis by Hupp et al.[1] To prepare Pd/NH<sub>2</sub>-UiO-66, 0.5 g of vacuum dried NH<sub>2</sub>-UiO-66 was suspended in 50 mL of methanol followed by the addition of 30 mg of PdCl<sub>2</sub> in 1 mL aqueous HCl solution and stirred at RT for 12 h. The resultant solid was isolated by centrifugation, dried at 80 °C and finally reduced with 0.1M NaBH<sub>4</sub> aqueous solution. For the transfer hydrogenation of NB to AN, 0.05 g of Pd/NH<sub>2</sub>-UiO-66 in 5 mL H<sub>2</sub>O was introduced into a 15 mL capacity ACE pressure tube, followed by the addition of 1

mmol of NB and 3.5 mmol of FA. The reactor tube was sealed and stirred at 60 °C for 7 h. After reaction, the products were extracted with ethyl acetate and quantitatively analyzed by Agilent 6890 GC with a DB-5 column.

Fig. 1 represents the catalytic transfer hydrogenation scheme over Pd/NH<sub>2</sub>-UiO-66. Fig. 2(a) displays the characteristic peaks of at  $2\theta = 7.34^\circ, 8.48^\circ$  of the highly crystalline NH<sub>2</sub>-UiO-66 sample. The deconvolution of the Pd 3d XPS spectrum results in two peaks at 335.39 and 340.78 eV, which can be attributed to the Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>, confirming the existence of metallic Pd. The effect of reaction time on nitrobenzene CTH is shown in Fig. 2(b). When the reaction time increased from 1 to 7 h, the concentration of AN increases from 0.06 to 0.19 mmol/mL. Further increase to 8 h, very low concentration 0.01 mmol/mL of N-formyl aniline (FAN) was formed. Pd/NH<sub>2</sub>-UiO-66 achieved the NB conversion of 98% and AN selectivity 99% with FA in water at 60 °C after 7 h. With an increase in the FA to NB molar ratio, i.e., 2 to 3, the NB conversion increased from 68% to 86% with constant AN selectivity of 99%, which may be due to increased availability of H<sub>2</sub> generated through decomposition. No substantial efficiency loss in the hydrogenation of NB, at least for three repeated cycles was detected. Finally, a plausible reaction mechanism was proposed for the transfer hydrogenation reaction.

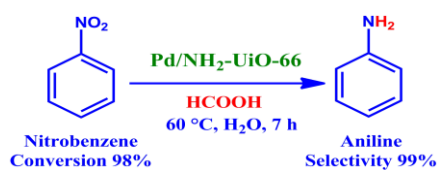


Fig.1 Reaction scheme of CTH of NB.

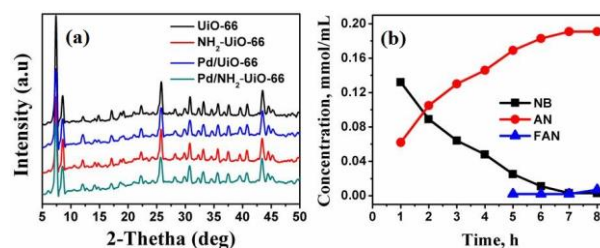


Fig.2 (a) XRD patterns of various samples and (b) Effect of reaction time on CTH of NB.

## REFERENCES

[1] M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, Chem. Commun., 49 (2013) 49, 9449.