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Chiral crystalline organic salts as supports of Pd nanoparticles forming selective heterogeneous catalysts for hydrogenation of nitroarenes

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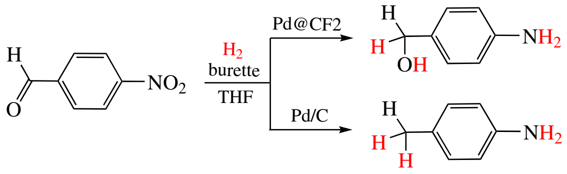
A novel catalyst based on Pd nanoparticles encapsulated in a chiral crystalline organic salt matrix is prepared from tetrasodium tetrakis(4-sulfonatophenyl)methane and tetrakis[4-(*S*)-prolinamidophenyl]methane in water at room temperature under hydrogen atmosphere. The hydrogenation of *p*-nitrobenzaldehyde over this catalyst stalls at the stage of *p*-aminobenzyl alcohol, whereas Pd/C brings the reduction further to *p*-toluidine.



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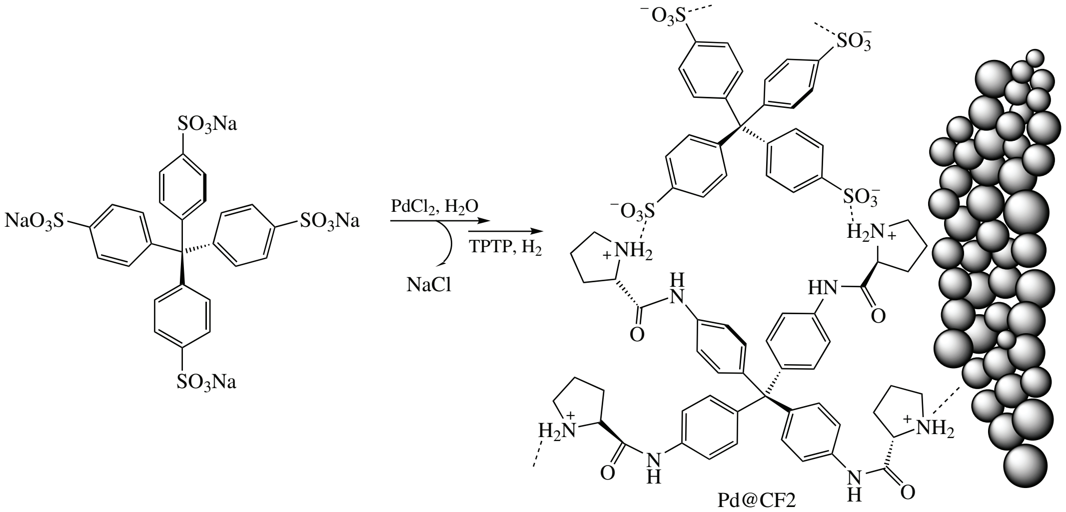
The global industrial production of consumer goods relies heavily on catalytic methods, amongst which the heterogeneous catalysts are employed in 80% of chemical processes, including very important hydrogenation reactions.[1,2] The heterogeneous catalysts employing bulk metal or metal nanoparticles supported on solid carriers are easy to recover, and the arrangement is robust.[3,4] Particularly significant case is the catalytic hydrogenation of nitroaromatic compounds with cheap and ecologically friendly molecular hydrogen.[5,6]

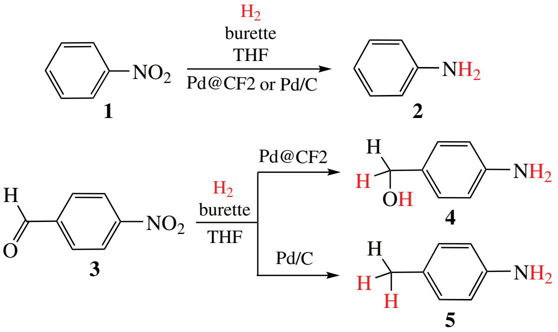
However, the classical heterogeneous hydrogenation performance suffers from inherent low selectivity towards different reducible groups present in the same substrate[6] or undesired side reactions in case of multistage reduction reactions such as in cases of nitro compound.[7] We believed that organic self-assembled sterically uniform crystalline salts[8] would provide cheap carriers for nanoparticles with added possible selectivity of their performance.

In this work we report the synthesis of a chiral tecton, tetrakis[4-(*S*)-prolinamidophenyl]methane tetrakis(hydrotrifluoroacetate) (*S*)-TPPM (see Online Supplementary Materials, Scheme S1). Its further reaction with tetrasodium tetrakis(4-sulfonatophenyl)methane (TSPM) preliminarily agitated with PdCl$_2$ gave crystalline organic porous salt CF2. In this manner, Pd nanoparticles were entrapped into CF2 to afford heterogeneous catalyst Pd@CF2 (Scheme 1) with 13% of Pd.



Scheme 1

The catalytic performance of Pd@CF2 was tested in hydrogenation of some nitroarenes (Scheme 2). The catalytic reduction of nitrobenzene **1** to aniline **2** at a ratio of the substrate to Pd 100 : 1 (calculated on all the Pd present) proceeded cleanly with ‘as prepared’ catalyst without any side reactions at room temperature and atmospheric pressure with TOF 50–60 h^{-1} in THF. Under similar conditions, Pd@CF2 had the same catalytic activity as Pd/C (Alfa Aesar, 5% Pd) if both were previously activated under H_2 at 50 °C. The heterogeneous catalyst Pd@CF2 was recyclable, at least, up to 5 times and not pyrophoric. The true heterogeneity of the catalysis with Pd@CF2 was proved by an interrupted experiment of the reduction of nitrobenzene **1**. There was no catalytic activity associated with a reaction mixture which was filtered to remove the heterogeneous catalyst after 1 equiv. of H_2 had been consumed. Leaching of palladium into the solution was also tested by ICP-MS analysis which indicated that only 0.5% of the metal went into a solution of nitrobenzene reduction.



Scheme 2

No aggregation of the nanoparticles was observed in the course of the reaction according to BF-STEM measurements (see Online Supplementary Materials, Figure S1). The mean diameter of palladium NPs in the material isolated after catalytic hydrogenation was approximately 2.1 nm, and the particle size distribution was relatively narrow (standard deviation was ~0.5 nm). Apparently, one of the functions of CF2 was physically protecting the nanoparticles from cintering.

The catalyst was also selective as compared with Pd/C. For example, *p*-nitrobenzaldehyde **3** was reduced to *p*-aminotoluene **5** with H_2 on Pd/C and predominantly (>80%) to *p*-aminobenzyl alcohol **4** if promoted with Pd@CF2 (see Scheme 2 and Figure 1).

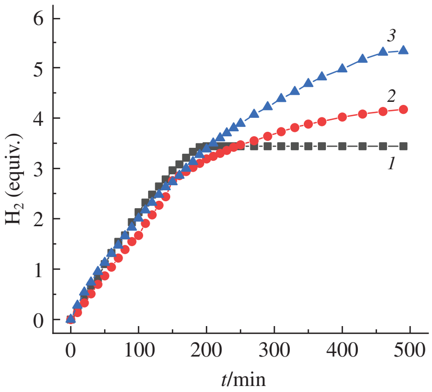


Figure 1 Catalyzed hydrogenation of the following nitroarenes in THF: (*1*) nitrobenzene **1** over Pd@CF2, (*2*) *p*-nitrobenzaldehyde **3** over Pd@CF2 and (*3*) *p*-nitrobenzaldehyde **3** over Pd/C.

In conclusion, a novel type of chiral supramolecular frameworks has been designed and implemented for the stabilization of metal nanoparticles. Interesting selective catalytic properties of the material have been found.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.014.

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