Mesoporous Au-TiO_2 nanoparticle assemblies as efficient catalysts for the chemoselective reduction of nitro compounds

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Synthesis of aromatic amines by selective hydrogenation of aromatic nitro compounds has emerged as one of the most important and, synchronously, challenging task in synthetic organic chemistry. Amines are highly valuable intermediate chemicals particularly used in the manufacture of pharmaceuticals, polymers, dyes and cosmetics. Although various noble metal nanoparticles (NPs) supported on a metal oxide, such as Au/CeO_2, Pt/Al_2O_3 and Au/Fe_2O_3, have been successfully used to reduce nitroaromatic compounds, these catalysts require harsh reaction conditions and are characterized by poor selectivity [1]. The selective hydrogenation of nitro into amine groups is not trivial because of the unavoidable formation of azo- and azoxy-derivatives during the reaction process. Therefore, exploring new catalytic systems offering high chemoselective production of aromatic amino-compounds is an ongoing research.

Gold supported on TiO_2 is the most promising catalyst for hydrogenation or oxidation of alkene, carbonyl and nitro compounds. In this work, we demonstrate novel mesoporous Au-sensitized TiO_2 as high-effective catalysts for the selective transformation of nitroaromatics into the corresponding amines. Namely, we utilized deposition-precipitation of gold hydroxides within the pores of mesoporous TiO_2 nanoparticle ensembles (MTA) [2]. The obtained materials (Au-MTA) possess a continuous network of interconnected gold and anatase TiO_2 (ca. 9 nm) nanoparticles with controllable gold particle size (i.e. ranging from 3 to 10 nm) and exhibit large and accessible pore surface area (ca. 100–160 m^2/g), as evidenced by SAXS, XRD, TEM and N_2 physisorption measurements [3]. Interestingly, Au-MTA show outstanding performance for the selective reduction of nitro into amine groups using sodium borohydride as reducing agent. We also addressed the role of supported gold particles on the chemoselective response of Au-MTA, showing that the yield and product composition are highly related to the Au loading and particle size. As a result the 2% Au-MTA catalyst associated with 5-nm-sized Au nanoparticles has found to be a prominent catalyst for the reduction of nitroaromatics, not only giving exceptionally high selectivity (>96%) and conversion yield (>92%) to the corresponding amines, but also allowing the efficient synthesis of aromatic amino-compounds at ambient conditions.

References

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