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PdO/CuO Nanoparticles on Zeolite-Y for Nitroarene Reduction and Methanol Oxidation

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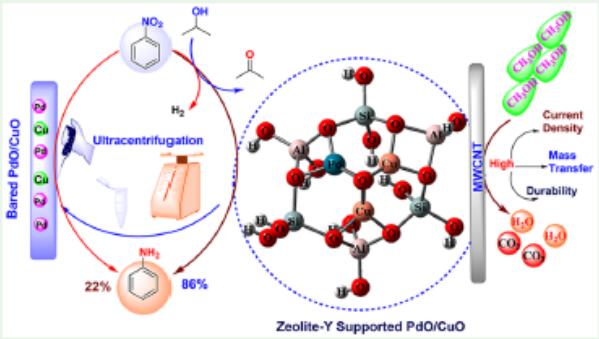
Supporting Information

ABSTRACT: Selective reduction of various nitroarenes to amines was achieved up to 93% under autoclave condition in isopropanol using catalytic amount of palladium oxide/copper oxide (PdO/CuO) nanoparticles (NPs) supported on mesoporous zeolite-Y, PdO/CuO-Y. The catalyst was also found to be highly effective for one-pot cascade synthesis of the 3,3′-diaminobiphenyl from 3-nitrophenylboronic acid (NPBA). The hybridization of PdO/CuO-Y with multiwalled carbon nanotubes (MWCNTs) resulted in a highly effective and durable electrocatalyst for the methanol oxidation reaction (MOR). The mass activity of the electrocatalyst was found to be 690 A/g and was stable for 4000 s. The catalytic activity of the PdO/CuO-Y catalyst was found to be superior in terms of productivity and recyclability in comparison to that of the bared PdO/CuO NPs separated by the ultracentrifugation (UC) method. On the other hand, the one modified with the carbon matrix retained the same activity and reduced the reaction time in nitroarene reduction reaction (NAR) under identical conditions. Electrochemical studies and density functional theory (DFT) calculations were performed to understand the mechanism of the NAR process. Both the experimental and theoretical evidence explicitly demonstrated the individual role of both palladium (Pd) and copper (Cu). Pd was found to be the active site for nitroarene interaction, while CuO NPs played an important role in isopropanol oxidation.



KEYWORDS: *PdO/CuO-Y, bared PdO/CuO NPs, ultracentrifugation, nitroarene reduction, methanol oxidation reaction*

1. INTRODUCTION

Zeolite-Y is considered to be one of the important classes of crystalline aluminosilicates because of its high surface area and suitable pore openings.[1] Because this zeolite-Y has been used as a suitable host for encapsulation or immobilization of various homogeneous catalysts.[2,3] The advantages of such a heterogenization approach are in recyclability, selectivity in the reaction, and thermal stability of the catalyst.[1−3] The other zeolitic type materials, such as MCM-41 and SBA-15, are also used as hard templates for the synthesis of fine nanoalloys.[4,5] Out of the various types of bimetallic nanoalloys those containing palladium (Pd) and copper (Cu) have recently found high attention because of their ability to convert various catalytic reactions with high turnover frequency or number (TOF, TON) and efficiency.[6,7] A large number of reports are available in the literature on the synthesis and applications of such nanomaterials.[8,9] Although the reported nanocatalysts were effective, most of them failed in terms of recyclability, lose control over self-agglomeration, and thereby, hamper the catalytic activity. Zeolite-Y is known to be thermally stable and also to control the growth of metal-oxide nanoparticles (NPs).[1,8] Therefore, it will be beneficial if such kind of bimetallic nanoalloys could be synthesized on zeolite-Y using it as support, as well as an internal hard templating agent.[4,5] Recently, palladium oxide (PdO)/copper oxide (CuO) and PdO/nickel oxide (NiO) NPs of smaller dimensions have been synthesized using zeolite-Y as self-templating agent for C−Cl bond activation and benzyl alcohol oxidation reactions.[8,10]

Nitroarene reduction (NAR) is one of the important reactions that are known to be catalyzed by Pd- and Cu-containing catalyst in the presence of external reducing agents like sodium borohydride ($NaBH_4$) or hydrazine (NH_2NH_2).[11−13] Cui et al.[6] found 93% yield of anilines using $NaBH_4$ and Pd-Cu-NPs supported on carbon. Similarly,

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