Recyclable Copper Nano-catalyst for the Selective Oxidation of Benzene to *p*-Benzoquinone (*p*-BQ) using H_2O_2(aq) in CH_3CN

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Abstract

The molecular copper complex tetrakis(acetonitrile)copper(I) perchlorate [Cu(CH3CN)4ClO4] was shown to act as a catalyst precursor for the efficient oxidation of benzene to *p*-benzoquinone (*p*-BQ) with a percentage selectivity of 60−80% under mild conditions, and produces phenol (PhOH) as a minor product at room temperature. The formation of copper based nanoparticle catalyst (NC) from tetrakis(acetonitrile)copper(I) perchlorate [$Cu(CH_3CN)_4ClO_4$] to be the vital step responsible for its ability to catalyze the conversion of benzene to *p*-BQ. The copper NC easily formed *in situ* through the oxidation of substrate using H_2O_2 in CH_3CN. After separating the NC from the reaction mixture and recycling them several times, it still maintained comparable catalytic efficiency and selectivity for the conversion of benzene to *p*-BQ. Characterization of the Cu NC was performed using X-ray absorption spectroscopy (XAS) and electron paramagnetic resonance (EPR) techniques to examine the structural insights for the molecular assembly in the metal clusters. From the surface analysis study of XPS, together with the Cu XAS study, for Cu NC, we identify this oxide materials is mainly consisted as copper oxide where the identified functional groups of Cu^{+}–O, Cu^{2+}–O and Cu^{2+}–OH suggest the catalytic oxidation from benzene to *p*-BQ and PhOH mainly involve the chemistry between Cu^{+} and Cu^{2+}. From XAS data analysis, both oxygenated trinuclear copper cluster and CuO_x ($x \sim 1$) were used as a structural model for extended X-ray absorption fine structure (EXAFS) fitting. The Cu NC with copper core structure consisted of ~2–3 copper ions could remotely cluster together with a high homogeneity and act as the major component in Cu NC for the selective oxidation of benzene to *p*-BQ catalytically. In addition to this, the solid-state EPR spectra at 77 and 298K investigation exhibited that in Cu NC a copper cluster in a cupric state exist.

Keywords - copper; nanoparticle; oxidation; catalysis; hydrogen peroxide.