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Heterogeneous catalytic activity of the $[Cu(bpy)_2]^{2+}$ complex supported in silica-coated magnetic nanoparticles

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The development of bioinspired metal complexes that can act as models for the galactose oxidase (GOase) attracted much attention, and many of those compounds have been synthesized and characterized [1]. This enzyme catalyzes the oxidation of primary alcohols to the corresponding aldehydes with strict regioselectivity. A typical organic substrate employed to test the GOase-like activity by model complexes is the benzyl alcohol (BnOH) [2]. In fact, industrially benzaldehyde (BA) is strategically relevant and finds applications in spices, pharmaceuticals, adhesives, and dyes. Inorganic platforms for heterogeneous catalysts employed in BnOH oxidation has been described, and among them, are the SiO_2-coated magnetic Fe_3O_4 nanoparticles. This approach is very convenient to rapidly separate/retrieve the catalyst from the mother solution by applying an external magnetic field when the catalytic process is over. Fe_3O_4 nanoparticles also present desirable features such as biodegradability, biocompatibility, practicality, and low preparation cost [3]. Here, we present the catalytic oxidation of benzyl alcohol (BnOH) mediated by the $[Cu(bpy)_2]^{2+}$ complex anchored in Fe_3O_4@SiO_2 magnetic nanoparticles. The complex $[Cu(bpy)_2](ClO_4)_2$ (**1**) and the Fe_3O_4@SiO_2 magnetic nanoparticles were prepared according to methods already described [3,4]. The metal complex was characterized by elemental analysis, FTIR and UV-Vis spectroscopies, molar conductivity and cyclic voltammetry while each step of the magnetic nanoparticles preparation was followed by TEM/EDS, powder DRX and DLS techniques. When **1** was incorporated at the Fe_3O_4@SiO_2 (followed by UV-Vis spectroscopy) a 4.4% of immobilization was obtained to afford the catalyst **1**-Fe_3O_4@SiO_2. Using 1 mol% of catalyst, 20-fold of H_2O_2 (oxidant) over the substrate (BnOH) during 24 h of reaction, 5.46%±0.31 of conversion was observed. After three rounds reusing the catalyst, the cumulative conversions reached 11,8%, which is 60% higher than the homogeneous studies (7.34%±0.33), probing its recyclability. Radical scavenging tests with TEMPO did not affect substrate conversions, indicating that no radical species were involved in the catalysis. Finally, the chemical selectivity for BA was 100% once no benzoic acid (BzA) was detected during the catalytic studies. Future studies point towards a deeper analysis into the mechanistic pathways for the catalytic oxidation of the BnOH mediated by **1**-Fe_3O_4@SiO_2.

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