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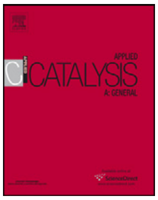

Copper(II) complexes of arylhydrazones of β-diketones immobilized on Zn–Al layered double hydroxides as effective recyclable catalysts for peroxidative oxidation of alkanes

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ABSTRACT

New Cu^{II} complexes $[Cu(H_2O)(\mu\text{-}L^1)Na(H_2O)]_n\cdot 2nH_2O$ (**4**), $[Cu(H_2O)(\mu\text{-}HL^2)Na(H_2O)]_n\cdot 2nH_2O$ (**5**) and $[Cu(H_2O)(\mu\text{-}L^3)Na(H_2O)]_n\cdot 2nH_2O$ (**6**), bearing the SO_3^- or COO^--functionalized arylhydrazones of β-diketones (AHBDs) 3-(2-hydroxy-3-sulfo-5-nitrophenylhydrazone)pentane-2,4-dione (H_3L^1, **1**), 3-(2-hydroxy-3,5-disulfophenylhydrazone)pentane-2,4-dione (H_4L^2, **2**) or 1-ethoxy-2-(2-hydroxy-4-carboxyphenylhydrazone)butane-1,3-dione (H_3L^3, **3**), were synthesized and characterized by elemental analysis, IR spectroscopy, ESI-MS and X-ray analysis (for **4**). **4**–**6** were immobilized on the layered double hydroxides (LDH) $[Zn_{0.74}Al_{0.26}(OH)_2](NO_3)_{0.26}\cdot 0.23H_2O$ and characterized by X-ray powder diffraction patterns (XRPD), UV–vis, IR spectroscopies, thermogravimetric (TG) and differential thermal (DTA) analyses. The heterogenized Cu^{II}AHBD-LDH systems catalyze the peroxidative oxidation (with TBHP or H_2O_2 as oxidant) of alkanes (cyclohexane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane) mainly to alcohols, under mild conditions, and can be recycled at least five times without significant loss of activity, with overall yields of 10–15% per cycle depending on the catalyst used. Regioselectivity at position 2 of the alkane is favoured by the heterogenized catalysts.

1. Introduction

Layered double hydroxides (LDHs), also called anionic clays or hydrotalcite-like materials, have brucile-type layers consisting of M^{2+} ions surrounded by octahedrally coordinated hydroxo ligands [1–13]. When some M^{2+} ions are isomorphically substituted with M^{3+} ions, a positive layer net charge is induced and compensated by the anions in the interlayer. Thus, a general formula for such LDHs can be presented as $[M^{2+}{}_{(1-x)}M^{3+}{}_x(OH)_2][A^{m-}{}_{x/m}]\cdot nH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Zn^{2+}, Mg^{2+} and Al^{3+}, Cr^{3+} respectively, and A^{m-} is a simple or complex organic or inorganic anion, such as Cl^-, NO_3^- or CO_3^{2-}. LDHs have been used as supports in heterogeneous catalysis as their structures can allow an effective catalyst immobilization by multiple electrostatic interactions together with covalent bonds and hydrogen bonding. Moreover, generally LDHs have other interesting features, being resistant to oxidation, easy to prepare, insoluble in a wide range of solvents, can be easily recovered from the reaction medium, *etc.*

Recently, it was demonstrated that Cu^{II} complexes of arylhydrazones of β-diketones (AHBDs) can be used as effective catalysts for some reactions, in particular alkane or alcohol oxidations [14,15]. However, until now the Cu^{II}AHBD catalysts have been studied only under homogeneous conditions, and no attempts to immobilize them and perform an effective recyclization were reported. It can be expected that introduction of $-SO_3^-$ or $-COO^-$ groups into the AHBD ligands would create a possibility for immobilization on a LDH matrix by, *e.g.*, hydrogen-bonding and electrostatic interactions (Fig. 1).

The direct mild catalytic oxidation of alkanes into valuable products is a hot topic due to the potential use of the former as rich carbon feedstocks for highly demanded synthesis of oxidized organic products and the possibility to overcome a number of energy- and time-consuming steps in their preparation [16–21]. Several Cu^{II} complexes were found to be rather effective *homogeneous* catalysts for such oxidation [14,15,22–32], but not much was done to facilitate their separation and recycling. The *heterogeneous* catalysts applied for this reaction commonly are expensive (*e.g.*, gold nanoparticles), exhibit low activities and selectivities towards

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