Improved NO_x removal by visible light photocatalysis trough ZnAlEu layered double hydroxides

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Currently there is huge concern to address the NO_x gases pollution ($NO + NO_2$), due to their hazardous effects on citizen health and environment. The concentration of these gases can be reduced directly from the air at ppb levels in cities through photocatalytic technology (De-NO_x process), by using the sunlight irradiation and a photocatalyst at soft conditions. Nevertheless, this technology is not extended enough mainly because of commercial photocatalysts (TiO_2-based) are active only under UV light, not taking advantage of the visible light (about 43 % of the received solar energy), resulting in low NO_x removal efficiencies[1].

Layered Double Hydroxides (LDHs) are interesting materials due to its high photocatalytic De-NO_x selectivity[2], low cost and chemical tuneability[3]. Herein, ZnAl-LDHs were doped with small amounts of Eu^{3+}. In order to keep a "green" scope, the synthesis was carried out by a simple coprecipitation method, at room temperature, with water as a the only solvent and without using complex apparatuses. The substitution of Al^{3+} by Eu^{3+}, cations with quite different atomic radii, should induce some disorder in the LDH structure, which might improve its photocatalytic efficiency.

The samples were characterised to analyse their structure, porosity, morphology, optical and electronic properties. The results showed that Eu incorporation in LDH layers decreased its crystallinity, also producing a *110* plane reflection shifting, confirming the Eu doping. The optical band gap was decreased with the Eu^{3+} content, and the electronic bands of the compounds were modified, as observed by VB-XPS. The photocatalytic NO_x removal efficiency of the doped samples was improved. Additionally, the optimal Eu-doped LDH showed a De-NO_x efficiency under visible irradiation (420 nm) of ~ 47 %, overcoming the activity of the undoped LDH (~ 12 %). In addition, the optimal photocatalyst virtually maintained its high removal efficiency for long irradiation tests (up to 18 h), the photocatalyst being stable and reusable after those tests. The enhanced NO_x removal efficiency is related to a lessening of the electron/hole recombination (confirmed by PL) and an improved generation of ·OH radicals (confirmed by EPR spin-trapping experiments), resulting from the unusual position of Eu in the LDH framework and its electronic configuration. The positive results open the door to use these doped LDHs for other photocatalytic applications where the harvesting of visible light is a key.

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