PhD THESIS

LAYERED DOUBLE HYDROXIDE-BASED CATALYSTS FOR FINE ORGANIC SYNTHESIS

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ABSTRACT

Layered double hydroxides, a family of anionic clay minerals, have frequently aroused the curiosity of the scientific community due to their distinctive lamellar structure and versatility in composition. Creating layered double hydroxide solids with different cation or anion compositions and tracking how these variations alter the structural, textural, and catalytic capabilities of the materials are the primary goals of the current thesis. The structural and textural properties were analyzed using various techniques, while the catalytic performances were verified in different fine organic syntheses.

The original part of the thesis starts with a study regarding the influence of the preparation method – co-precipitation and mechanochemical – on the physico-chemical properties and the catalytic activity of Ce-modified LDH structures having a part of the trivalent cations, namely aluminum, replaced with cerium. The resulting layered double hydroxides and their corresponding mixed oxides were catalytically tested in different types of condensation reactions: first, in the self-condensation of cyclohexanone and, then, in the Claisen-Schmidt condensation, where compounds belonging to the flavonoid class, namely chalcone and flavone, were synthesized. The mechanochemical route of preparation has enabled the elimination of some steps, equipment and energetic consumption required in the co-precipitation method. The synthesized compounds exhibited the hydrotalcite structure, as indicated by the XRD measurements, whatever the preparation method used. However, apart from a ceria minor phase present in both of them, in the co-precipitated LDH material a supplementary side phase, i.e. cerium oxycarbonate, was identified.

The mixed oxide derived from the LDH prepared by the mechanochemical method show larger surface area, lower real and bulk densities, higher basicity and lower acidity compared with that obtained from the co-precipitated LDH material.

The LDH materials have comparable activities in cyclohexanone self-condensation, but significantly lower compared to their corresponding mixed oxides. Among the latter, the mechanochemically prepared oxide was slightly more active than its co-precipitated counterpart. In all cases, the mono-condensation product 2-cyclohexylidencyclohexanone was the main reaction product, with selectivities of 76-84 % for the LDH catalysts, and 86-88 % for the LDH-derived mixed oxides. The mechanochemically prepared oxide showed good stability during four reaction cycles.

In the Claisen-Schmidt condensation reactions, the mechanochemically prepared oxide catalyst was also shown to be more efficient than its co-precipitated counterpart, obviously due to its higher number of base sites. At the same time, both oxides showed good selectivities to the desired product, the mechanochemically prepared oxide catalyst being slightly more selective to chalcone and flavone.

The previous LDH solid containing cerium prepared by co-precipitation was modified further with graphene oxide (GO), resulting in a sandwich-like compound. The LDH-GO composites, which bear different concentrations of GO in the range of 5-25 wt. %, were tested as catalysts in two other organo-chemical transformations: the Knoevenagel condensation between benzaldehyde and diethyl malonate and the tandem aerobic oxidation of benzyl alcohol followed by Knoevenagel condensation of the obtained benzaldehyde with benzoyl acetonitrile. The co-precipitation of $Mg_3Al_{0.75}Ce_{0.25}$ LDH in the presence of a GO suspension led to HT3Ce-xGO composites with increased crystallinity as indicated by the XRD analysis. The diffractograms of the composites also showed that no other impurities could be found besides the CeO_2 phase. Raman spectroscopy clearly highlighted the existence of GO in the HT3Ce-xGO composites, while the SEM images demonstrated that the elementary particles were grouped either in layered polymorphic particles with edges,"ovoidal" composite particles or cubic agglomerates, and the amount of ovoidal particles increased with GO content. Using the parent solids HT3Ce and GO, the conversions obtained were rather low compared to the hybrid composites. On the other hand, a synergistic effect between the LDH and GO parent materials present in the HT3Ce-xGO composites, leading to improved catalytic activity was noticed. In the Knoevenagel condensation, the catalytic activity of the hybrids increased with the GO content in the composite catalysts up to an optimum for

HT3Ce-15GO system, then it decreased for higher GO contents. In the case of the tandem reaction, the conversion of benzyl alcohol was higher for the hybrid HT3Ce-xGO systems compared to the LDH and GO materials alone, the latter being completely inactive, but it decreased with the increase of the GO concentration.

To observe the effect on the catalytic performance of the LDH-GO hybrid not only when the Mg3Al brucite-like layers are modified by inserting another cation like cerium, but also when the interlayer space contains other anions, like molybdate, the neat Mg3Al-LDH was modified with molybdate anions (MoO_4^{2-}) and with graphene oxide in the range of 5-25 wt.%. The solids were tested, as in the previous case, in the one-pot cascade oxidation-Knoevenagel condensation. Compared to the HT3Ce-xGO hybrids, when the brucite-type layer was modified with another cation like cerium, the situation changed when the interlayer of the LDH was modified with molybdate, namely, the conversion increased with the increase of the GO concentration.

To open up new perspectives in the rational design of efficient bifunctional catalytic systems, several samples were prepared by inserting in the brucite-like layers various metallic cations having different molar ratios. The study involved the synthesis of multicationic MgNi(Cu)Al-layered double hydroxides using the co-precipitation method. Practically, three series of catalysts were prepared, having the following general formulas: $Mg_{1.2}Ni_aCu_bAl(OH)_6(CO_3)_{0.5}$ (a+b=0.8), $Mg_{0.8}Ni_cCu_dAl(OH)_6(CO_3)_{0.5}$ (c+d=1.2), and $M_2Al(OH)_6(CO_3)_{0.5}$ (where M is Ni or Cu). All three series were characterized and tested catalytically in the one-pot cascade oxidation-Knoevenagel condensation reaction. The calcined forms of the $Mg_{1.2}Ni_aCu_bAl(OH)_6(CO_3)_{0.5}$ (a+b=0.8) and $M_2Al(OH)_6(CO_3)_{0.5}$ (where M is Ni or Cu) series were also tested in Payne oxidation reaction of cyclohexene. For the LDH samples modified with nickel and copper, the alcohol conversion and the product yield varied with the loading of nickel: the higher the amount of Ni, the higher the values of conversion and yield. It can be sustained that all the LDH materials acted as bifunctional catalysts.

In the case of the mixed oxide solids derived from the hydrotalcites, the catalytic results in the Payne oxidation showed that the highest cyclohexene conversion was obtained for the compound containing both nickel and copper cations, suggesting a synergetic interaction between the two divalent cations.

To check the importance of the copper cation inserted in the brucite-type layers of the LDH, samples containing cobalt instead of copper were created. Thus, three series having the following general formulas $Mg_{1.2}Ni_aCo_bAl(OH)_6(CO_3)_{0.5}$ (a+b=0.8), $Mg_{0.8}Ni_cCo_dAl(OH)_6(CO_3)_{0.5}$

(c+d=1.2), $M_2Al(OH)_6(CO_3)_{0.5}$ (where M is Ni or Co) were prepared and tested as catalysts in the one-pot oxidation-Knoevenagel condensation reaction. The results obtained were inferior compared to the solids containing copper.