Speciation Level Differences in the Structure of Three Mg-Al-CO_3 Layered Double Hydroxides Prepared by Alkoxide and Alkoxide-Free Sol-Gel Syntheses, and Hydrothermal Precipitation

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Layered double hydroxides (LDHs), called also anionic clays or hydrotalcites, are complex hydrous oxides built on the layers with a brucite-like structure carrying a net positive charge that is balanced by the anions intercalated between the positively charged layers. The chemical compositions of their layer cations and their interlayer anions can be greatly varied, and the interlayer space can be explored for many applications such as removal of target ions/molecules from water, catalysis, medicine, drug delivery, cosmetics etc. However, after being discovered more than 170 years ago, in two major applications based on the interfacial phenomena, adsorption and catalysis, the application of LDHs at the industrial scale have not been found. The main producing companies of LDHs sell them as plastic additives and PVC stabilizers [1-2]. To explain this phenomenon, the structure, surface chemistry, and anion adsorptive properties of the three Mg-Al LDHs produced by different (yet advanced) methods of synthesis have been compared in [3]. The studies were conducted on the speciation level to demonstrate how different the properties of LDHs are if prepared by various synthetic methods.

Application of greater than usual number of research tools for characterisation of the structure, surface chemistry and mechanism of adsorption demonstrated that the three Mg-Al-CO_3 LDHs differed in their porous/layered structure (N_2 adsorption, CO_2 sorption,) crystallinity (XRD), speciation of Al (NMR) and Mg (XPS), thermal stability (TGA), hydration (TGA, FTIR), the interlayer carbonate (FTIR), morphology (SEM) and Mg/Al ratio on the surface and in bulk. Commercial LDH (Sasol company, Germany) [2] produced by traditional alkoxide sol-gel method had poor speciation parameters, the lowest surface area and hydration. Hydrothermally precipitated LDH had an intermediate structure/surface properties desired for adsorbents. Alkoxide-free sol-gel generated LDH (a purely fine inorganic synthesis) had the highest surface area and CO_2 sorption, hydration, variety of ionic carbonate and Al/Mg species. These differences were reflected in their adsorptive performance and stability in water solutions comparing to the materials shown in the literature. In addition to exceptional adsorptive removal properties towards toxic anions (target anions for water industry) the LDH prepared by the original alkoxide-free sol-gel method [4-7] produces unique material which is the only LDH that keeps its layered structure after thermal treatment until 600 ^{o}C while all other LDHs shown in the literature lose their layered structure at 300 ^{o}C. This unique property (when double oxide produced from layered double hydroxide is still layered material) in combination with rich speciation can open new avenues in many industrial applications of LDHs if prepared by this synthetic approach.

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