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Editorial: Layered double hydroxides and their use as catalysts in sustainable processes

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Editorial on the Research Topic
Layered double hydroxides and their use as catalysts in sustainable processes

Introduction

Layered double hydroxides (LDH) are solids that belong to the anionic clays class with the general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}\cdot[A_{x/n}]^{n-}\cdot mH_2O$, where M^{2+}, M^{3+} and A^{n-} represent divalent and trivalent metal cations and inorganic/organic anions respectively with m number of interlayer water molecules. Pure LDH-type materials require values of x ($M^{3+}/M^{2+} + M^{3+}$) between 0.2 and 0.33. The LDH as well as their corresponding mixed oxides obtained by calcination of the parent LDH at temperatures up to 500°C–600°C, continue to be of great interest due to the properties presented (Cavani et al., 1991): i) the ability to insert in an uniform distribution of different cations in the octahedral positions of the layered structure as well as different types of anions in the interplanar space; ii) tailored textural properties; iii) acid/base active site presence (ditopic properties); iv) high surface area; v) memory effect (reconstruction of the layered structure by hydration with solutions containing different anions), etc., All of the above listed properties makes these materials find their utility in a wide variety of fields, e.g., environment protection (Abd El-Monaem et al., 2023); catalysis (Farhan et al., 2024); catalytic support (Baskaran et al., 2015), medicine and pharmacy (Yang et al., 2017), industry (Zhai et al., 2022), adsorbents (Yang et al., 2016), etc., All these areas of interest are based on the peculiar physico-chemical properties presented by LDH-type materials generated in a simple way by the traditional synthesis methods: co-precipitation, sol-gel, ion-exchange, hydrothermal, urea hydrolysis, microwave irradiation as well as memory effect (Farhan et al., 2024), and non-traditional methods, e.g., microwave (Zadaviciute et al., 2017), electro-synthesis (Molano-Mendoza et al., 2018), thin films via electrophoretic technique (Kim et al., 2008), mechano-chemical (Tongamp et al., 2007), etc., The LDH structure is similar to that presented by $Mg(OH)_2$ where the isomorphic replacement of Mg^{2+} cation with a trivalent one (*except* V^{3+} *and* Ti^{3+} *which are not stable in air*), with a similar radius [*0.72Å in charge II and coordination VI* (Shannon, 1976)], leads to the formation of positively charged sheets, which are balanced by the presence of compensating anions placed in the interlayer space. Water molecules are present in all unoccupied places. Furthermore, the LDH layered structure is not limited to the presence of the Mg^{2+} cation, but any other divalent cation with a radius similar to that of magnesium, which can adopt the octahedral structure leads to the generation of LDH-type materials. The synthesis of these types of layered materials involving monovalent cations is limited only to lithium (*ionic radius 0.76Å; charge I; coordination VI*), the other monovalent cations, e.g., Na^+; K^+; NH_4^+, despite the fact that they accommodate in octahedral positions, have too large ionic radii [$Na^+ = 1.02Å$; $K^+ = 1.38Å$; $NH_4^+ = 1.67Å$ (Shannon, 1976)], leading to the obtaining of dawsonite-type materials.

The current Research Topic entitled "*Layered Double Hydroxides and their Use as Catalysts in Sustainable Processes*" aims to highlight and promote articles involving new approaches for the synthesis of LDH-type materials, modern techniques for characterizing their physicochemical properties and the evaluation of catalytic activities in various chemical reactions.

Seliverstov et al. emphasize in the mini review the most important studies regarding the synthesis and catalytic applications of LDH-type materials containing rare earth cations. Thus, a number of catalysts have been considered in different catalytic processes: i) Mg/AlLn LDH (Ln = Ce, Sm, Dy, and Yb) were synthesized by co-precipitation and considered in methane oxidation; ii) Ni/FeGd LDH by hydrothermal synthesis used in oxygen evolution; iii) Ni/FeTiLa LDH was synthesized by pulsed-laser ablation in liquids for the electrocatalytic water oxidation; iv) mixed oxides of Ni/AlCe via LDHs precursors synthesized by the urea hydrolysis for optimal catalytic activity in steam reforming of glycerol for H_2 production; v) Ni/La LDH with N-doped graphene by sonochemical method for hydrogen evolution reaction; vi) Ni/FeCe LDH electrocatalyst by electrodeposition technique for water splitting; vii) Mg/Al + La LDH by mechanochemical synthesis for cyclohexene conversions; etc., Also, other systems have been considered such as: Mg/AlTb LDH; Mg/Tb LDH; Mg/AlEu and Ca/AlEu LDHs; Zn/AlGd LDHs; Zn/AlDy LDH; Zn/AlCe LDHs; Mg/AlEu LDH, etc., The authors also proposed a direction in which promethium, holmium, thulium, and lutetium are considered to be inserted into the octahedral structure of LDH despite the fact that promethium exhibits radioactive behavior. Also, binary RE-LDHs catalysts including samarium, europium, thulium, and ytterbium are of great interest.

In the same year, 2022, Charalambous et al. used a trivalent rare earth cation, i.e., La as well as K, to promote Ni/MgAl LDH for catalytic conversion of CO_2 to CH_4. The lanthanum-promoted Ni catalysts sample showed 89.3% in catalytic activity compared to that of unmodified sample (10Ni/MgAl) of 33.4%, while potassium-promoted samples presented a similar conversion with that of unmodified one. However, in terms of CO selectivity that increased from 35.7% to 62.0%. The beneficial effect of Ni/MgAl doping with La and K was materialized by increasing the Ni dispersion together with improving of the Ni reducibility, which was reflected in the CO_2 conversion and product selectivity values. Considering the similar approach, Mane et al. (2024) investigated the production of long-chain (straight and branched) ketones by direct α-alkylation of short chain ketones using both homogenous and LDH-type catalysts in water as solvent. Thus, produced long-chain ketones are fuel precursors and can subsequently be hydrogenated to long-chain alkanes suitable for blending in aviation and liquid transportation fuels. The catalytic activity of Ni and Pd metals supported on layered double oxides as solid base materials was compared with 5%Pd/$BaSO_4$ with NaOH as the base additive, using α-alkylation of 2-butanone with 1-propanol as an exemplar process, where both metal and base sites are necessary for the selective conversion of 2-butanone to alkylated ketones. Amongst the solid base catalysts, 5%Pd/C with 5% Ba/hydrotalcite showed the optimum result with 51% 2-butanone conversion and 36% selectivity to the alkylated ketones, while 2.5% Ni/$Ba_{1.2}Mg_3Al_1$ exhibited comparatively lower catalytic activity with 21% conversion of 2-butanone and 47% selectivity to alkylated ketones.

Dalma et al. considered conversion of glycerol to glycerol carbonate as an interesting chemical reaction for evaluation of catalytic behavior of mixed oxides obtained by calcination of LDH that included Cu, Zn, or Ni as modifying cations of MgAl hydrotalcite in a percentage of 15%. This reaction required the base active sites, high surface area, homogeneous cation dispersion, but also a thermal stability of material. In mild reaction conditions, solvent free as well as 1:2 ratio of glycerol:ethylene carbonate, yields higher of 80% were obtained due to univorm distribution of base sites and optimal textural property. Among the 3 modifiers, Cu proved to be the best in catalytic terms.

In 2023, Sushkova et al. prepared hexacyanoferrate intercalated Mg-Al LDH as a novel smart corrosion sensing coating. The catalyst synthesis was based on the idea that hexacyanoferrate ions are sensible to react with iron cations generated during the corrosion process while LDH can provide a controlled release of active ions from interlayer space under corrosion conditions. The authors considered two types of coatings, one based on epoxy and the other on polyurethane, which improved the barrier properties of the coating without affecting the corrosion detection functionality of the detection layer. Standard salt spray tests were also performed.

The extensive body of research surrounding LDH-based materials underscores their versatility and applicability across a wide range of strategic fields. Numerous studies have not only validated the effectiveness of these materials but also highlighted their potential in areas such as catalysis, environmental remediation, drug delivery, and energy storage. The low production costs and facile scale up further reinforces that LDH-based materials have significant potential both in scientific and industrial domains. As research continues to unveil innovative ways to harness their versatile structural properties, it is evident that the utilization of LDHs will expand, positioning them as key players in future technological advancements and sustainable solutions.

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