catalysts

Editorial

# Layered Double Hydroxide-Based Catalytic Materials for Sustainable Processes

**Ioan-Cezar Marcu * and Octavian Dumitru Pavel ***

Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018 Bucharest, Romania
* Correspondence: ioancezar.marcu@chimie.unibuc.ro (I.-C.M.); octavian.pavel@chimie.unibuc.ro (O.D.P.)

Layered double hydroxides (LDH) or hydrotalcites (HT), together with their corresponding mixed oxides, continue to arouse a great deal of research interest. Due to their amazing properties [1], they are highly appreciated in various fields such as catalysis [2–7], pharmacy [8,9], medicine [10–12], environmental protection [13–15], etc. All the applications of LDH-based materials are due to their specific properties, which can be tailored by their composition and the synthesis methods employed for their preparation. Traditionally [16], the co-precipitation method provides a fast synthesis path with very high yields, wherein salts containing the targeted cations are contacted with an alkaline solution. Additionally, the traditional preparation methods for LDH include ion-exchange, rehydration using the structural memory effect, the hydrothermal method, and secondary intercalation. Currently, there are alternative methods for obtaining LDH-based materials including electrochemical synthesis, exfoliation in an aqueous solution, dry exfoliation, and the mechano-chemical method. These methods can be used to obtain LDH-based materials with peculiar physicochemical characteristics and, hence, specific properties, including excellent catalytic performances.

This Special Issue, entitled "Layered Double Hydroxide-Based Catalytic Materials for Sustainable Processes" is a collection of 12 articles, including one review paper, presenting the preparation of different LDH-based materials, their physicochemical characterization, and the study of their catalytic performance in various chemical reactions.

In their review paper, Stamate et al. [17] emphasize the most relevant studies related to the large group of polyoxometalate (POM)-intercalated LDH solids, with a focus on their synthesis, characterization, and catalytic applications. Althabaiti et al. [18] bring to bear new information about CoMgAl-LDH used in Michael addition of an aryl halide compound onto activated olefin as a Michael acceptor. The ultrasound was found to have a beneficial effect on this reaction due to the cavitation phenomenon. Zn is a widely used cation in obtaining LDH-type materials with photocatalytic applications. Therefore, by two different methods, Trujillano et al. [19] prepared Zn,Al-layered double hydroxides as well as their corresponding mixed oxides by calcination at 650 °C, to be used in adsorption and photocatalytic degradation of 4-nitrophenol in an aqueous solution. Here, the mixed oxides display a better performance in the adsorption/degradation of the contaminant than ZnO, also showing the memory effect. Zăvoianu et al. [20] present a study of the influence of chemical composition of $Zn_xAl$- and $Mg_xAl$-LDH ($x = 2$–$5$) and $Mg_yZn_zAl$-LDH ($y + z = 4$, $y = 1, 2, 3$) on the olefin epoxidation with $H_2O_2$ in the presence of acetonitrile. It was found that the catalytic activity and the basicity of the samples varies in the order LDH ($OH^-/CO_3^{2-}$) < Reconstructed LDH (majority $OH^-$) < Calcined LDH ($O^{2-}$), and the yield to epoxycyclohexane increases almost linearly when the number of weak and medium-strength base sites in the brucite-type layer rises in the range 4.5–8.5 mmol·g$^{-1}$. The same author and coworkers [21] synthetized MgZnAl-LDH by a nontraditional mechano-chemical method in the presence of an organic base, tetramethylammonium hydroxide, with good activity in Claisen–Schmidt condensation between benzaldehyde and cyclohexanone. Indeed, conversions higher than



**Citation:** Marcu, I.-C.; Pavel, O.D. Layered Double Hydroxide-Based Catalytic Materials for Sustainable Processes. *Catalysts* **2022**, *12*, 816. https://doi.org/10.3390/catal12080816

Received: 20 July 2022
Accepted: 21 July 2022
Published: 25 July 2022

90% after 2 h of reaction with a total selectivity toward 2,6-dibenzylidenecyclohexanone were observed. Korolova et al. [22] study the effect of Al, Ga, Fe, and In trivalent $M^{3+}$ cation from $Mg_6M^{3+}{}_2(OH)_{16}CO_3 \cdot 4H_2O$ in aldol condensation between furfural and acetone. The authors conclude that the catalytic performance of the rehydrated mixed oxides is determined by the "host" MgO component, rather than by the nature of $M^{3+}$. Dib et al. [23] provide further evidence that LDH-type materials can play an important role in environmental protection, using CuAlCe ex-LDH mixed oxides in the total oxidation reactions of both toluene and ethanol. The authors claim that the sample with the highest content of Ce showed the best catalytic properties due to the improvement of the reducibility of the copper species and their good dispersion on the surface. In the same vein of environmental processes, Argote-Fuentes et al. [24] use active hydrotalcites in the degradation of Congo red dye through processes assisted by ultraviolet (UV) irradiation and electric current, where maximum degradation was reached with the photoelectrocatalytic process with active hydrotalcites and a copper anode at 6 h with 95% in a half-life of 0.36 h. Additionally, Nayak et al. [25] degraded visible light-triggered Rhodamine B in the presence of MgCr-LDH nanoplatelets with an efficiency of 95% at 0.80 $kW/m^2$ solar light intensity in 2 h. Additionally, Wang et al. [26] oxidized the formaldehyde with air at low temperature in presence of Mn-containing mixed-oxide-supported bismuth oxychloride (BiOCl), and showed that the complete removal of formaldehyde could be achieved at 70 °C, the removal efficiency being maintained more than 90% for 21 h. Another application of LDH catalysts is the transesterification reaction. Tajuddin et al. [27] studied the catalytic activity of NiAl-layered double hydroxides in tributyrin transesterification with methanol. The activity of the calcined-rehydrated NiAl-LDH materials was found to increase with Ni content and corresponding base site loadings. Huang et al. [28] obtained metallic Ni by reducing a Ni precursor in a $H_2$ atmosphere at 500 °C for 3 h dispersed on an ex-LDH LiAl mixed oxide deposited on an Al structured framework, i.e., lathe waste strips. This supported catalyst was studied in ethanol steam reforming (ESR). The relatively low acidity of the ex-LDH LiAl oxide support led to low activity for the dehydration of ethanol and high activity for $H_2$ generation.

All these studies clearly show that LDH-based materials have a great number of applications as catalysts and catalyst supports for a broad range of chemical reactions which are of interest and importance for the sustainable development of our society. This being the case, future development in the research of LDH-based materials looks set to continue.

Finally, we thank the *Catalysts* journal for this great opportunity to produce this Special Issue. We also thank both the authors and the referees for their hard work and contribution to the success of this Special Issue.

**Author Contributions:** Conceptualization, I.-C.M. and O.D.P.; writing—original draft preparation, I.-C.M. and O.D.P.; writing—review and editing, I.-C.M. and O.D.P.; visualization, I.-C.M. and O.D.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Cavani, F.; Trifiro, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today* **1991**, *11*, 173–301. [CrossRef]
2. Sahoo, D.P.; Das, K.K.; Mansingh, S.; Sultana, S.; Parida, K. Recent progress in first row transition metal Layered double hydroxide (LDH) based electrocatalysts towards water splitting: A review with insights on synthesis. *Coord. Chem. Rev.* **2022**, *469*, 214666. [CrossRef]
3. Gabriel, R.; de Carvalho, S.H.V.; da Silva Duarte, J.L.; Oliveira, L.M.T.M.; Giannakoudakis, D.A.; Triantafyllidis, K.S.; Soletti, J.I.; Meili, L. Mixed metal oxides derived from layered double hydroxide as catalysts for biodiesel production. *Appl. Catal. A* **2022**, *630*, 118470. [CrossRef]
4. Heravi, M.M.; Mohammadi, P. Layered double hydroxides as heterogeneous catalyst systems in the cross-coupling reactions: An overview. *Mol. Divers.* **2022**, *26*, 569–587. [CrossRef] [PubMed]

5. Tichit, D.; Álvarez, M.G. Layered Double Hydroxide/Nanocarbon Composites as Heterogeneous Catalysts: A Review. *ChemEngineering* **2022**, *6*, 45. [CrossRef]
6. Álvarez, M.G.; Marcu, I.-C.; Tichit, D. Recent Innovative Developments of Layered Double Hydroxide-Based Hybrids and Nanocomposite Catalysts. In *Progress in Layered Double Hydroxides—From Synthesis to New Applications*; Nocchetti, M., Costantino, U., Eds.; World Scientific: Singapore, 2022; Chapter 4; pp. 189–362.
7. Marcu, I.-C.; Urdă, A.; Popescu, I.; Hulea, V. Layered Double Hydroxides-based Materials as Oxidation Catalysts. In *Sustainable Nanosystems Development, Properties, and Applications*; Putz, M.V., Mirica, M.C., Eds.; IGI Global: Hershey, PA, USA, 2017; Chapter 3; pp. 59–121.
8. Zhang, L.-X.; Hu, J.; Jia, Y.-B.; Liu, R.-T.; Cai, T.; Xu, Z.P. Two-dimensional layered double hydroxide nanoadjuvant: Recent progress and future direction. *Nanoscale* **2021**, *13*, 7533–7549. [CrossRef]
9. De Sousa, A.L.M.D.; dos Santos, W.M.; de Souza, M.L.; Barros Silva, L.C.P.B.; Koo Yun, A.E.H.; Aguilera, C.S.B.; de França Chagas, B.; Araújo Rolim, L.; da Silva, R.M.F.; Rolim Neto, P.J. Layered Double Hydroxides as Promising Excipients for Drug Delivery Purposes. *Eur. J. Pharm. Sci.* **2021**, *165*, 105922. [CrossRef]
10. Kankala, R.K. Nanoarchitectured two-dimensional layered double hydroxides-based nanocomposites for biomedical applications. *Adv. Drug Deliv. Rev.* **2022**, *186*, 114270. [CrossRef]
11. Rojas, R.; Mosconi, G.; Zanin, J.P.; Gil, G.A. Layered double hydroxide applications in biomedical implants. *Appl. Clay Sci.* **2022**, *224*, 106514. [CrossRef]
12. Choi, G.; Choy, J.-H. Recent progress in layered double hydroxides as a cancer theranostic nanoplatform. *WIREs Nanomed. Nanobiotechnol.* **2021**, *13*, e1679. [CrossRef]
13. Dong, Y.; Kong, X.; Luo, X.; Wang, H. Adsorptive removal of heavy metal anions from water by layered double hydroxide: A review. *Chemosphere* **2022**, *303*, 134685. [CrossRef] [PubMed]
14. Ye, H.; Liu, S.; Yu, D.; Zhou, X.; Qin, L.; Lai, C.; Qin, F.; Zhang, M.; Chen, W.; Chen, W.; et al. Regeneration mechanism, modification strategy, and environment application of layered double hydroxides: Insights based on memory effect. *Coord. Chem. Rev.* **2022**, *450*, 214253. [CrossRef]
15. Zhang, G.; Zhang, X.; Meng, Y.; Pan, G.; Ni, Z.; Xia, S. Layered double hydroxides-based photocatalysts and visible-light driven photodegradation of organic pollutants: A review. *Chem. Eng. J.* **2020**, *392*, 123684. [CrossRef]
16. He, J.; Wei, M.; Li, B.; Kang, Y.; Evans, D.G.; Duan, X. Preparation of Layered Double Hydroxides. *Struct. Bond.* **2005**, *119*, 89–119.
17. Stamate, A.-E.; Pavel, O.D.; Zavoianu, R.; Marcu, I.-C. Highlights on the Catalytic Properties of Polyoxometalate-Intercalated Layered Double Hydroxides: A Review. *Catalysts* **2020**, *10*, 57. [CrossRef]
18. Althabaiti, N.S.; Al-Nwaiser, F.M.; Saleh, T.S.; Mokhtar, M. Ultrasonic-Assisted Michael Addition of Arylhalideto Activated Olefins Utilizing Nanosized CoMgAl-Layered Double Hydroxide Catalysts. *Catalysts* **2020**, *10*, 220. [CrossRef]
19. Trujillano, R.; Nájera, C.; Rives, V. Activity in the Photodegradation of 4-Nitrophenol of a Zn,Al Hydrotalcite-Like Solid and the Derived Alumina-Supported ZnO. *Catalysts* **2020**, *10*, 702. [CrossRef]
20. Zăvoianu, R.; Cruceanu, A.; Pavel, O.D.; Bradu, C.; Florea, M.; Bîrjega, R. Green Epoxidation of Olefins with $Zn_xAl/Mg_xAl$-LDHCompounds: Influence of the Chemical Composition. *Catalysts* **2022**, *12*, 145. [CrossRef]
21. Zăvoianu, R.; Mihăilă, S.-D.; Cojocaru, B.; Tudorache, M.; Pârvulescu, V.I.; Pavel, O.D.; Oikonomopoulos, S.; Jacobsen, E.E. An Advanced Approach for MgZnAl-LDH Catalysts Synthesis Used in Claisen-Schmidt Condensation. *Catalysts* **2022**, *12*, 759. [CrossRef]
22. Korolova, V.; Kikhtyanin, O.; Veselý, M.; Vrtiška, D.; Paterová, I.; Fíla, V.; Capek, L.; Kubička, D. On the Effect of the $M^{3+}$ Origin on the Properties and Aldol Condensation Performance of $MgM^{3+}$ Hydrotalcites and Mixed Oxides. *Catalysts* **2021**, *11*, 992. [CrossRef]
23. Dib, H.; El Khawaja, R.; Rochard, G.; Poupin, C.; Siffert, S.; Cousin, R. CuAlCe Oxides Issued from Layered Double Hydroxide Precursors for Ethanol and Toluene Total Oxidation. *Catalysts* **2020**, *10*, 870. [CrossRef]
24. Argote-Fuentes, S.; Feria-Reyes, R.; Ramos-Ramírez, E.; Gutiérrez-Ortega, N.; Cruz-Jiménez, G. Photoelectrocatalytic Degradation of Congo Red Dye with Activated Hydrotalcites and Copper Anode. *Catalysts* **2021**, *11*, 211. [CrossRef]
25. Nayak, S.; Parida, K. MgCr-LDH Nanoplatelets as Effective Oxidation Catalysts for Visible Light-Triggered Rhodamine B Degradation. *Catalysts* **2021**, *11*, 1072. [CrossRef]
26. Wang, X.; Wu, G.; Ma, Y. Low-Temperature Oxidation Removal of Formaldehyde Catalyzed by Mn-Containing Mixed-Oxide-Supported Bismuth Oxychloride in Air. *Catalysts* **2022**, *12*, 262. [CrossRef]
27. Tajuddin, N.A.; Manayil, J.C.; Lee, A.F.; Wilson, K. Alkali-Free Hydrothermally Reconstructed NiAl Layered Double Hydroxides for Catalytic Transesterification. *Catalysts* **2022**, *12*, 286. [CrossRef]
28. Huang, S.-H.; Chen, Y.-J.; Huang, W.-F.; Uan, J.-Y. Electrodeposition of a Li-Al Layered Double Hydroxide (LDH) on a Ball-like Aluminum Lathe Waste Strips in Structured Catalytic Applications: Preparation and Characterization of Ni-Based LDH Catalysts for Hydrogen Evolution. *Catalysts* **2022**, *12*, 520. [CrossRef]