



Review Highlights on the Catalytic Properties of Polyoxometalate-Intercalated Layered Double Hydroxides: A Review

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Abstract: Layered double hydroxides (LDH) are an extended class of two-dimensional anionic materials that are known for their unique lamellar structure, versatile composition, and tunable properties. The layered architecture allows the intercalation between the positively charged sheets of a vast variety of anionic species, including oxometalates and polyoxometalates (POM). The hybrid composites that were developed using POM and LDH show great advantages when compared to both parent materials causing the appearance of new functionalities, which may lead to remarkable contributions in many areas of application, especially in catalysis. The current review paper emphases all of the crucial works already existing in literature that are related to the large group of POM-LDH solids and their use as catalysts for fine organic synthesis. The new trends in the development of the POM-LDH catalysts are highlighted based on the overview of 121 scientific articles that were published between 1984 and 2019. The main topics are focused primarily on the synthesis, characterization, and the catalytic applications of different LDH systems hosting polyoxometalates with low, medium, and high nuclearity. The intense exploration of the POM-LDH field has led to the obtaining of countless effective catalysts used in various types of reactions, from condensation, esterification, halodecarboxylation, to oxidation and epoxidation.

Keywords: layered double hydroxides (LDH); polyoxometalates (POM); catalytic materials

1. Introduction

As the Earth is constantly changing, society has also become driven by ever-increasing requests. The constant need to fulfill the existing demands represents the main priority of the scientists throughout the world. Catalysis has been the key point of our industrialized society, playing a crucial role in the development of the world's economy, allowing for the conversion of raw materials into valuable fine chemicals, in an environmentally friendly and low-cost manner [1]. Catalysts are suitable for applications in a variety of areas (industry, agriculture, environment, ecology, etc.), and it has been estimated that almost 90% of all chemical processes are based on catalysis [1]. This increasing, ongoing need for selective catalysts has enabled the discovery of a series of novel catalytic materials.

Layered double hydroxides (LDH), which are also known as hydrotalcites, are anionic compounds that currently receive increasing attention, owing to their special lamellar structure and other unique properties that make them suitable for applications in several different advanced technological processes: pharmaceutics synthesis, drug delivery, photochemistry, electrochemistry, and many others. Nevertheless, their main application area is in catalysis, either as precursors, catalyst supports, or catalysts. Many of these chemical transformations require stoichiometric amounts of the liquid base for conversion to the desired product, making them economically and environmentally inefficient, so their replacement with hydrotalcite-like catalysts is crucial. From the structural point of view, hydrotalcites can be described as lamellar solids having each layer positively charged with negatively charged interspace species. A wide variety of anionic species can be interlayered either during the formation of the lamellar structure, or by anion exchange [3]. Consequently, layered double hydroxides offer a remarkable opportunity for synthesizing new intercalated composite materials, having improved chemical properties due to a synergistic effect.

Polyoxometalates (POMs) are a versatile group of compounds that contain different transition metal cations, such as Mo, W, V, Nb, etc. at their highest oxidation states. Their properties have been widely exploited in a variety of areas, including catalysis, medicine, pharmaceutical industry, and electronics, due to their variable composition, sizes, rich redox chemistry, and charge distribution [4]. Hybrid materials that are developed using POM and layered double hydroxides have invoked a great deal of interest lately due to their unique properties, also exhibiting advantages over both parent materials, especially in catalytic applications. Several intermolecular interactions, such as electrostatic and hydrogen bond networks, can be established between the brucite-like layers of the hydrotalcites and the intercalated polyoxometalates anions [4]. Additionally, the confinement effect that is displayed by the hydrotalcite interlayer gallery prevents the polyoxometalate anionic species from leaching into the reaction mixture, while also increasing the selectivity of the catalytic transformation [4].

Herein, a complete survey of the scientific literature related to the expanded family of POM-LDH composite materials and their use as catalysts for fine organic synthesis is presented. The main topics will be focused on the synthetic approaches that were developed until nowadays for obtaining different polyoxometalates (POM) that were intercalated within layered double hydroxides. The characterization of these materials, the changes induced in their properties (as compared to those displayed by the same anions in the bulk form), and their catalytic applications are also scrutinized.

2. Layered Double Hydroxides (LDH)-Generalities

Layered double hydroxides (LDH), which are the most known representatives of the anionic clays, are a large family of two-dimensional (2D) materials intensively studied due to their unique catalytic properties conferred by their variable composition [5]. Structurally, layered double hydroxides can be described as lamellar compounds that are similar to brucite, in which every Mg^{2+} ion is octahedrally surrounded by six hydroxyl ions and shares edges to form infinite sheets of $Mg(OH)_2$ [6]. These sheets are overlapping, yielding a layered architecture that is held together by hydrogen bonds or by van der Waals forces [6]. The octahedral coordination of the metals in the layers can be modified if the radius of the cations becomes larger. This can happen when one side of the octahedron is open towards the interlamellar domain with the obtaining of a supplementary coordination of one interlamellar water molecule [4]. If a part of the Mg^{2+} ions is replaced by trivalent cations having a similar ionic radius, such as Al^{3+} or Fe^{3+} , then the entire layer will have a positive charge density. The electrical neutrality of the LDH type solids is maintained by the anions that occupy the interlayer positions (Figure 1).



Figure 1. Structural representation of layered double hydroxides (LDH). Adapted from Ref. [4], Copyright 2017, MDPI.

There are two possibilities to stack the layers, either with a rhombohedral (3R symmetry) or a hexagonal cell (2H symmetry). The 3R symmetry is attributed to the hydrotalcite compounds, while the 2H is known as manasseite [4]. Layered double hydroxides are described by the following general molecular formulas: $[M(II)_{1-x}M(III)_x(OH)_2][A^{m-}_{x/m}\cdot nH_2O]$ or $[M(I)_{1-x}M(III)_x(OH)_2][A^{m-}_{(2x+1)/m}\cdot nH_2O]$ [7], where M⁺ (M: Li), M²⁺ (M: Mg, Ni, Co, Zn), and M³⁺ (M: Al, Cr, Fe, In, etc.) are metallic cations that are connected with each other through the hydroxyl groups, in a cationic layer, A^{m-} represent the anions, which, along with m molecules of water, form the anionic layer and x is the charge density or the anionic exchange capacity and it takes values between 0.15–0.5 [8]. It can be calculated while using the formula: x = M(III)/(M(III) + M(II)) [3].

The anionic species that can be introduced between the LDH layers can be grouped in the following families of compounds [9]:

- halides;
- non-metal oxoanions;
- oxo- and polyoxometallate anions;
- anionic complexes of transition metals;
- organic anions; and,
- anionic polymers.

It is possible to obtain a large variety of synthetic hydrotalcites-like compounds by simply adjusting their chemical composition in what concerns the nature and proportion of the cations, the nature of the counter ion, or the synthesis conditions that may influence the amount of water in the interlayer region or the crystal morphology and size [10]. Therefore, there is a great possibility to synthesize the materials that fulfill the demands that are specific for different catalytic applications.

2.1. LDH-Preparation Methods

Layered double hydroxides can be synthesized in aqueous medium employing a variety of methods, depending on the specific requirements and the desired properties. The most frequently used is the co-precipitation, which implies mixing the aqueous solutions of precursors (divalent and

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trivalent metal salts, in well-defined proportions) with an alkaline solution containing the precipitating agent (Na_2CO_3 , NH_4Cl , NaOH), which has the role of maintaining a constant pH value to enable the co-precipitation of the mixed hydroxide [11]. A variety of techniques can also be applied for the preparation of the layered double hydroxides, including urea hydrolysis, hydrothermal synthesis, the sol-gel method, and microwave synthesis [12]. These are the most common and widely used solution-phase methods for hydrotalcites synthesis.

Another technique that can be used for both the preparation of LDH and for intercalation purposes is the mechanochemical method. The principle of this method is based on the idea that the precursor salts under the conditions of the mechanical treatment undergo a chemical reaction that results in the formation of the LDH [11]. Given that the formation of the LDH takes place in the solid state, there is no need for aging, which implies higher energy consumption and a longer duration process. Manual grinding or ball milling can be applied as pretreatment as a function of the nature of the precursor (metallic salts, oxides, hydroxides) to obtain uniform mixtures [13]. It has been demonstrated that it is better to utilize as raw materials metallic salts instead of stable hydroxides or oxides in manual grinding [9]. Zhang et al. [11,13] performed an investigation on the formation mechanism of LDH by manually grinding different metallic salts. They have observed that the raw materials disappeared immediately and a considerable amount of LDH phase appeared during milling when hydrated magnesium and aluminum nitrate salts are added into a mortar [13]. Three successive stages are involved in the process of grinding magnesium and aluminum nitrate hydrated salts with Na₂CO₃ and NaOH to form LDH: (i) absorption of water from the ambient air, (ii) formation of Al(OH)₃ and Mg(OH)₂, and (iii) the formation of LDH phases [13].

This method combines the advantages of both mechanochemistry and hydrothermal treatment, leading to high crystallinity of LDH at a relatively lower temperature or shorter reaction time when compared with the direct hydrothermal process, although the modality of producing is complex when compared with single solution operation [9].

The production of homogenous hybrid structures is a laborious process, therefore it is necessary to employ synthesis methods that present high applicability in terms of cost and environmental protection.

2.2. LDH-Applications

The LDH materials are mainly applied because of their base and redox properties that are present applications in various fields. Over the years, their properties and functionalities have been adjusted by employing different synthesis methods, design principles, and a wide range of metallic cations and organic or inorganic anions. They are often applied as supercapacitors, additives in polymers, or as adsorbents for water remediation [14], in the pharmaceuticals industry, in photochemistry [14], and in electrochemistry. In catalysis, hydrotalcites may be used as such or as mixed oxides obtained by their thermal decomposition, [5,12].

Their variable composition and their tunable intrinsic properties clarify the reason why catalytic usage belongs to their main field of applications. As solid base catalysts, LDHs exhibit high activities and selectivities for different types of reactions, mainly organic transformations (Figure 2), such as alkylation, isomerization, hydroxylation, transesterification, hydroformylation, redox reactions, condensation, and environmentally friendly reactions. Moreover, the mixed oxides that were obtained after calcination of the LDH usually have good catalytic activities and they have been applied to the following organic reactions: aldol and Knoevenagel condensations; epoxidation of olefins; halide exchanges; phenol hydroxylation; and, Michael additions [9].



Figure 2. Schematic representation of different organic transformations. Adapted from Ref. [3], Copyright 2015, Royal Society of Chemistry.

3. Synthesis of POM-LDH Nanocomposites

Polyoxometalates (POM) are an extended family of compounds that are obtained from the condensation of metal oxide polyhedra (MO_x , $M = W^{VI}$, Mo^{VI} , V^V , Nb^V , Ta^V etc., and x = 4 - 7) with each other through corner-, edge-, or, rarely, face-sharing manner [15]. Their synthesis is based on the similar charge to ionic radius ratio and charge density, which: (i) inhibits infinite polymerization; (ii) enables the formation of π -bonds with the O^{2-} ligands; and, (iii) leads to a diversity of coordination geometries [4]. The metal atoms are considered to be addenda atoms, because they can change their coordination with oxygen from four to six, while the MO_x polyhedra condense in solution upon acidification [15]. The nature of the ligand (water, hydroxo, or oxo species) dictates the limit of the polymerization. The nature and the number of the ligands depend on the solution pH and on the metal M^{n+} charge value. There were some POM clusters reported in the literature [15] that contain other atoms or groups, such as sulfur, bromine, nitrosyl, and alkoxy, although oxygen is the most known ligand that is capable of coordinating with the addenda atoms.

The cluster is called isopolymetalate, the Lindqvist type anion $[M_6O_{19}]^{2-}$ being representative when the POM framework consists of addenda metals (from groups 5 and/or 6) and oxygen (Figure 3). If the POM contains additional elements besides addenda metals and oxygen, it is known as a heteropoly complex, being formed by the condensation of MO_x polyhedra around a central heteroatom in acidic medium [15]. A large variety of atoms can act as heteroatoms, such as Be, B, Al, Si, Ge, Sn, P, Te, and the whole first row of transition elements. The atomic ratio between the surrounding atoms (referred to the addenda atoms) and the central heteroatom (arranged in tetrahedral or octahedral coordination) can be 6, 9, 11, or 12 [16]. These ratios come from the most common heteropoly compound structures. The most well-known and studied structure is the so-called Keggin with the general formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ (atomic ratio M/X = 12) [16]. POM compounds present high Brønsted acidity due to their large size, which leads to the delocalization of the surface charge density throughout the polyanion, creating a weak interaction between H⁺ and the anion. POM display not only high acidity, but also an efficient redox behavior, which conducts fast chemical transformations under soft conditions [16]. This makes POM highly efficient catalysts, especially in the oxidation reactions.



The large diversity of polyoxometalates compounds with well-defined structures offer huge adjustable possibilities for a variety of novel nanocomposite systems [4].

Figure 3. Polyoxometalates (POM) structures in polyhedral representations. Adapted from Ref. [15], Copyright 2013, Elsevier.

The POM/LDH materials have attracted wide interest in catalysis, as they have great advantages over other LDH-based compounds [4] that are attributed to the synergistic effects between the hydrotalcite and the polyoxometalates. The LDH solids offer a remarkable opportunity to modify their functionality without compromising their structural features due to the relatively weak interlayer interactions [4]. The incorporation of catalytically active species, such as inorganic anions, ligands, or biomolecules into the interlayer space of LDHs, has been proven to enhance the catalytic stability and recyclability when compared to their homogeneous counterparts [4]. A series of intermolecular interactions, including electrostatic and hydrogen bonding, can be found between the brucite-like layers of LDHs and the intercalated POM anions [15]. Figure 4 illustrates the general structure of the POM-LDH composition. Although POM-intercalated LDH exhibits superior application capabilities when compared to individual components, the intercalation of POMs into LDH implies some serious complications. First of all, under the neutral to slightly acidic reaction conditions, there is the possibility that $M^{2+/}M^{3+}$ cations leach out during the anionic exchange reactions between LDH precursor and the POM anions [15]. Secondly, the M²⁺/M³⁺ ratio in the POM pillared LDH must be rigorously controlled, since it helps to determine the charge density of the LDH layers, affecting the basal spacing between the brucite-type layers [10,15]. It is mandatory to maintain, as much as possible, the desired M^{2+}/M^{3+} ratio from the initial step of the preparation towards the final one in order to synthesize POM/LDH solids with different pore size distributions [15].



Figure 4. Structural representation of a POM/LDH. Adapted from Ref. [15], Copyright 2013, Elsevier.

It should be mentioned that, according to IUPAC rules [17], the main characteristic of intercalation compounds is the swelling of layered materials that appears when guest species are inserted in the interlayer region, while the term "pillared" should only be applied to the solids that were obtained by thermal or chemical transformation of a layered compound, which shows microporosity or mesoporosity and it is considered to be stable, both chemically and thermally [18]. This is not often the case of POM–LDH hybrids, which are thermally less stable than the compounds that were obtained, starting from cationic clays [18].

Moreover, some POM anions were proven to be unstable at weakly acidic to basic pH [15], explaining why the pillaring reactions are often accompanied by the co-formation of an impurity phase, consisting of the M²⁺ rich salt of the POM that deposits on the surface of the layered double hydroxide [15]. Its deposition can block the micropores of LDH, which leads to the obtaining of low surface areas [15]. It is difficult to prepare POM/LDH nanocomposites in a crystalline form, mostly because LDH hosts act like a base, while most polyoxometalates present acidic properties. Several synthesis methods can be used for the preparation of POM-LDH composites, the co-precipitation, the reconstruction, and the ionic exchange being among the most developed ones [4]. There are also some relatively new preparation techniques that still need improvements, such as electrochemical reduction, ultrasound treatment, and delamination technology [15].

The variety in what concerns the size and features of polyoxometalate compounds can be effectively used in the structural construction of new composite materials that display specific gallery height. Additionally, it is possible to access the gallery region by enlarging the lateral anion spacing if POMs with relatively high-charge density will be used in the construction of the hybrid materials. Therefore, POM can be viewed as ideal functional guest anions for intercalation offering the possibility of enhancing and fine-tuning the properties of the composite material might cause the appearance of new functionalities, leading to improved performance and offering the opportunity to increase many areas of application [4].

The POM/LDH hybrids have been intensively applied in catalytic reactions, such as epoxidation of alkenes, molecular oxygen generation, esterification of acetic acid, oxidation of thioether and thiophene, etc. [15]. The prepared POM-LDH composites show superior catalytic performance when compared to the relevant performance of their parent components. The active components are well dispersed in the two-dimensional enclosed space that is defined by the hydrotalcite layers. Moreover, the display of the robust interlamelar zone combined with the intermolecular interactions leads to an increased stability of the system, by preventing the leaching of the POM species into the reaction mixture [15]. The POM/LDH hybrid materials have also been used to enhance the photo-luminescent properties of lanthanide anions and promote the adsorption of harmful components, like dyes, from wastewater [15]. Recently, the delamination of LDH nanosheets has been employed before using them in the development of novel POM/LDH nanocomposite materials. This modern technology represents

the ideal solution for the above-stated problems while also retaining the original composition of POMs, apart from creating a new domain of application as photo-luminescent materials based on ultra-thin films [4].

Further investigations and the expansion of the family of POM-LDH composite materials will bring great opportunities in the development of economical and versatile methods for designing specific structural features that could lead reactions towards the desired path and will offer better control over their electron transfer properties [15]. Finally, the exploration of alternative design approaches will enable the construction of POM-LDH materials that present new chemical and physical properties, new types of functionalities, as well as a wider view of catalytic applications [15].

4. Systems Hosting Polyoxometalates

The main topic of this chapter is focused on the synthesis and catalytic activity of layered double hydroxides with a wide variety of cations in the layers, in relation to the nature of the intercalated anion; in this case, polyoxometalates with different nuclearity.

4.1. LDH Intercalated with Low-Nuclearity Polyoxometalates

There are only a few studies of chromate-containing LDH in the literature, and they are resumed in Tables 1 and 2. Cr(VI) in the forms CrO_4^{2-} and $Cr_2O_7^{2-}$ is among the most insidious anionic contaminants in wastewater, so the incorporation of chromates into layered double hydroxides deserves tremendous interest, not only because of their ability to protect the aquatic environment, but also for the valuable application in catalysis of the products obtained [18]. The reported methods used to synthesize LDH with intercalated chromate containing different pairs of divalent/trivalent cations in the brucite-like layers are co-precipitation, anion exchange, and reconstruction. Chromium can be introduced either as a cation, Cr(III) in the brucite-type layers [19–21] or it can be incorporated in its anionic forms CrO_4^{2-} and $Cr_2O_7^{2-}$ in the interlayer [21–30], mostly depending on the nature of the brucite-like cation. In most of the cases, the pairs of cations that were used for the construction of the novel composite materials were Mg-Al, Mg-Fe, Ni-Al, Ni-Fe, Zn-Al, Co-Al, and Ca-Al. A complete study on the use of calcined Mg-Al LDH containing chromium in three different structural sites: as Cr³⁺ in the brucite-like layers (A), as an intercalated Cr³⁺–EDTA complex (B) and as intercalated chromate (C), in non-oxidative dehydrogenation of ethane to ethylene (EDH), has been reported by Tsyganok et al. [21]. The synthetic strategies that were applied for preparing LDH precursors of chromium catalysts can be seen in Figure 5 and they consist of: (i) conventional co-precipitation of metal cations with carbonate counter-ion under basic conditions; (ii) co-precipitation of Mg(II) and Al(III) with a pre-synthesized EDTA chelate of Cr(III) (method based on the ability of Cr(III) to form a chelate of 1:1 stoichiometry with (EDTA)⁴⁻ that is much more thermodynamically stable than that of Mg(II) or Al(III) [21]); and, (iii) co-precipitation of Mg(II) and Al(III) with CrO_4^{2-} , chromate anions being present in the solution in slight excess to the amount that is required by stoichiometry. The powder XRD patterns of the materials synthesized by Tsyganok et al. [21] indicated that all of the samples had a layered structure specific to hydrotalcite compounds demonstrated by a set of characteristic diffraction lines at $2\theta = 11.3^\circ$, 22.8° , 34.4° , and 60.5° corresponding to reflections from (003), (006), (009), and (110) planes [21].

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	2	CrO_4^{2-}	Reconstruction	-	-	-	[22]
Mg,Al	3	CrO ^{-4²⁻}	Co-precipitation	-	-	-	[23,24]
Mg,Al	3	CrO ⁻ 4 ²⁻	Co-precipitation	EDH	Ethane	20	[21]
Mg,Al	3	Cr ^{III} (EDTA) ⁻	Co-precipitation	EDH	Ethane	21	[21]
Mg,Al	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[25]
Mg,Al	3	[Cr ^{III} (SO ₃ -salen)] ²⁻	Anion exchange	Oxidation	Benzyl alcohol	67–88	[28]
Mg,Al	3	[Cr ^{III} (SO ₃ -salen)] ²⁻	Anion exchange	Oxidation	Glycerol	30-32	[30]
Mg,Fe	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]
Mg,Fe	2	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[26]
Ca,Al	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]
Co,Al	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]
Co,Al	2	CrO ⁻ 4 ²⁻	Co-precipitation	Oxidation	Benzyl alcohol	23–34	[29]
Co,Fe	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]
Ni,Al	2.88	CrO ⁻ 4 ²⁻	Anion exchange	-	-	-	[27]
Ni,Al	2.83	$Cr_2O_7^{2-}$	Anion exchange	-	-	-	[27]
Ni,Fe	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]
Zn,Al	2	CrO ⁻⁴ ²⁻	Anion exchange	-	-	-	[22]
Zn,Al	3	CrO ⁻ 4 ²⁻	Co-precipitation	-	-	-	[23,24]

 Table 1. Summary of LDH with intercalated chromium-based anions.

Table 2. Summary of CrM-LDH (M-metal) with intercalated chromium-based anions.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Cu,Cr	2	CrO ^{-4²⁻}	Anion exchange	-	-	-	[19]
Cu,Cr	2	$Cr_2O_7^{2-}$	Anion exchange	-	-	-	[19]
Cu,Cr	2	CrO ^{-4²⁻}	Anion exchange	Alkoxylation	n-Butanol	43-49	[20]
Cu,Cr	2	$Cr_2O_7^{2-}$	Anion exchange	Alkoxylation	n-Butanol	72-83	[20]
Mg,Al,Cr	2;3	CO3 ²⁻	Co-precipitation	EDH	Ethane	20-21	[21]
Mg,Cr	2;3	CO3 ²⁻	Co-precipitation	EDH	Ethane	19–20	[21]



Figure 5. Synthetic approaches for the preparation of LDH precursors of chromium catalysts. Adapted from Ref. [21], Copyright 2007, Elsevier.

For the compound containing chromium pre-chelated with EDTA, the diffraction pattern obtained revealed that the d-spacing was similar with the reference hydrotalcite (i.e. 7 Å) containing only Mg and Al as cation, indicating that $Cr(EDTA)^-$ species were located at the external surface of the LDH crystallites, not in the interlamellar space. The comparison of the XRD pattern of the classical hydrotalcite with that of the LDH containing CrO_4^{2-} species in the interlayers showed that a phase with a larger d-spacing (i.e. 8.4 Å) was formed upon the co-precipitation of Mg(II) and Al(III) with chromate counter-ion, which suggested that the intercalation of the LDH with chromate anion led to an increase of the interlayer distance from 7.8 Å corresponding to the classical hydrotalcite to 8.4 Å for the intercalated LDH, which is in agreement with values that were reported in the literature [21]. On calcination at 500 °C partial oxidation to Cr^{6+} species was observed, and XPS indicated that the molar Cr^{6+}/Cr^{3+} ratio was always larger than 1.0. Ethane dehydrogenation (EDH) was studied at 700 °C during 5 h tests. The activity of all these catalysts significantly decreased, especially during the first hour, due to both the sintering and coking phenomena.

The solids that were synthesized by method (A) displayed the highest selectivity to ethylene (79–84%), but only with 12–15% ethane conversion, while larger conversions (26–30%) with lower selectivity (71–74%) were obtained for samples that were prepared by methods B and C [18]. The deposition of coke was the main problem during the catalytic tests, and its amount was quantified after tests by temperature-programmed oxidation (TPO) while using CO₂ as oxidant. The carbon content was very low (ca. 5%) for the Al-free catalysts [18,21]. After exposure to the EDH reaction and TPO experiments, it was observed that the specific surface areas of the solid sharply decreased, especially for the Al-free samples (ca. 75% decrease).

Wu et al. [28] used a different strategy, which consists first in the incorporation of the anionic salen-like ligand in the interlamellar space and then forming the complex in situ by reaction with Cr^{3+} chloride in order to incorporate chromium complexes in the interlayer of a Mg-Al LDH [28,30], as can be seen in Figure 6.



 $R = (CH_2)_2$; NH(CH_2CH_2)_2; orto-C₆H₄

Figure 6. The synthesis of MgAl-LDH with intercalated [Cr^{III}(SO₃-salen)]^{2–}. Adapted from Ref. [28], Copyright 2007, Elsevier.

The reported synthesis method applied for obtaining the sulphonato-salen chromium (III) ligand is the condensation reaction between salicylaldehyde and diamine. For the preparation, Wu et al. [28,30] have tried to use three different diamines (ethylenediamine, diethylenetriamine, and o-phenylenediamine), maintaining the molar ratio salicylaldehyde/amine around 2. The condensation products were further reacted with sulfuric acid to enable the formation of their corresponding phenyl sulfonated compounds, as seen in Step 2, Figure 6, and then with MgAl-LDH, which had the layers swelled by intercalation of benzoate anions.

Finally, the solid obtained was soaked with a CrCl₃ aqueous solution, leading to the formation of intercalated [Cr(SO₃-salen)]²⁻ complexes. The FTIR spectra of the three LDH-hosted chromium complexes indicated that the characteristic bands of $C_6H_5COO^-$ anions (1550 cm⁻¹) no longer appeared in the lamellar space of the LDH, which implied that they were completely exchanged with the $[Cr(SO_3-salen)]^{2-}$ anions. The powder X-ray diffraction patterns are characteristic of a veritable layered double hydroxide, also showing the formation of intensively swelled structures, with d₀₀₃ spacing of approximately 20 Å [28]. Wu and his group have published two articles [28,30], in which they have used the calcined solids as catalysts for the oxidation of different substrates, namely benzyl alcohol and glycerin while using H_2O_2 as oxidant. In the first case, the oxidation of benzyl alcohol led to selectivity for benzaldehyde lower than 80% for all of the prepared catalysts. Moreover, benzoic acid (ca. 15%) and benzyl benzoate (ca. 8%) were also formed. It was demonstrated that the catalytic performance of the three catalysts mostly depends on the diamine used, and it decreases depending the diamine backbones in the following sequence: $o-C_6H_4 > NH(CH_2CH_2)_2 > (CH_2)_2$ [30]. This decrease can be attributed to the different electronic structures and the steric effect of the three backbones [28,30]. Furthermore, $o-C_6H_4$ facilitated the contact of H_2O_2 with the active sites due to its planar structure. On the contrary, the other backbones ($NH(CH_2CH_2)_2$ and CH_2CH_2) that are both electron-donor groups led to an increase of the electronic density around the central metal ion hindering the formation of the oxochromium intermediate. Manayil et al. [29] have also studied the oxidation of benzyl alcohol at room temperature while using as catalyst a CoAl₂-LDH intercalated this time with chromate anions and tert-butyl hydroperoxide as oxidant. The results showed that an increase in the substrate/oxidant mole ratio will lead to 100% selectivity of benzaldehyde [29].

The LDH-intercalated sulphonato-salen-chromium(III) complex was also a good catalyst for the selective oxidation of glycerin to secondary alcohol-dihydroxyacetone (DHA) with 3% H_2O_2 probably due to the complementary effect that exists between the chromium-Schiff base complex and the weak base LDH host. The highest glycerin conversion reached 73.1%, with 43.5% of selectivity to DHA, when the reaction ran at 60°C for 4 h over 0.2 g catalyst with 25 mL 3% H_2O_2 . Moreover, the catalytic performance was maintained even after the catalyst was recycled six times [30].

Malherbe et al. [20] were able to prepare a series of POM/LDH nanocomposites by using Cr and Cu as the cations needed for the construction of the brucite-type layers and CrO_4^{2-} or $Cr_2O_7^{2-}$ as anions intercalated between the layers. The compounds have been tested in the catalytic ethoxylation of butanol by ethylene oxide to produce glycol ethers. The catalytic tests that were carried on in batch reactors have indicated that the catalytic activity of the solids is proportional to the concentration of chromium (VI), which should be theoretically present twice as much in the dichromate intercalated LDH. At maximum conversion, the selectivity is almost the same for both anions [20]. A detailed study of PXRD patterns has led to a better understanding of the ways the layers stack. MgAl–CrO₄ and MgFe–CrO₄ both showed a basal spacing of 10.8 Å and displayed turbostratic disorder [18]. Structural ordering of the first compound was induced by exposing it to a hydrothermal treatment. ZnAl-CrO₄ LDH also present stacking faults with local rhombohedral symmetry, but, in this case, the interlayer spacing was only 7.3 Å, which suggested that the chromate units were grafted to the hydroxyl layers. The MgAl–CrO₄ LDHs have proven to be more stable during calcination (up to 400 $^{\circ}$ C) than the ZnAl solids (300 °C) due to a fast formation of crystalline ZnO in the last case [25]. Spontaneous contraction of the layers can appear for ZnAl and ZnCr–LDHs that were intercalated with CrO_4^{2-} and/or $Cr_2O_7^{2-}$ after ageing, or even thermal treatment [31]. During ageing, for ZnAl-CrO₄ and ZnCr-Cr₂O₇, a decrease of the basal spacings from 8.61 to 7.86 Å and from 9.20 to 7.34 Å, respectively, appeared. Moreover, it was observed that the Cr(VI) species are more easily reduced to Cr(III) species in the ZnAl systems than in MgAl–CrO₄ ones [25]. Hydrotalcites containing Cu or Zn as cations in the brucite-type layers are not easily synthesized by the usual methods that are described in the literature [31], because their hydroxides do not have the brucite-like structure; instead, they are prepared by adding an aqueous solution of the trivalent cation salt to a suspension of the divalent cation oxide, followed by anionic exchange [31]. Further, NiAl–CrO₄, NiFe–CrO₄, CoAl–CrO₄, and CoFe–CrO₄ LDHs also

show turbostratic disorder as the examples aforementioned, maintained, even after exposure to a hydrothermal treatment where the purpose is to increase the crystallite size and favor grafting [18].

The environmental safety, ease of production, relatively low cost of precursors, and enhanced stability make it possible to suggest that layered double hydroxides intercalated with chromate, dichromate, and other different chromium-based anions, such as Cr^{III}(EDTA)[–] and [Cr^{III}(SO₃-salen)]^{2–} are promising materials, which are still under development and can be successfully used as catalysts, especially for oxidation reactions.

4.2. LDH Intercalated with Medium-Nuclearity Polyoxometalates: Vanadates and Molybdates

4.2.1. Vanadates

The vanadium-based anions were among the very first polyoxometalates to be successfully intercalated into layered double hydroxides structure. A wide range of polyoxovanadate ions can be inserted in the interlayer space, from discrete to polymeric anions. Although decavanadate is the most used, there are studies that are also devoted to the intercalation of lower oligovanadates. The pH influences the polymerization degree of the oxovanadates. A high nuclearity is associated to a decreased pH value, as seen in Table 3.

Table 3. The polymerization degree of oxovanadates versus pH. Information taken from Ref. [18].

pН	Oxovanadate Species Formed
1–3	Decavanadate $[V_{10}O_{26}(OH)_2]^{4-}$, $[V_{10}O_{27}(OH)]^{5-}$, $[V_{10}O_{28}]^{6-}$
4–6	Metavandate VO(OH) ₃ , VO ₂ (OH), [V ₃ O ₉] ^{3–} , [V ₄ O ₁₂] ^{4–}
8-11	Pyrovanadate [VO ₃ (OH)] ^{2–} , HV ₂ O ₇ ^{3–} , [V ₂ O ₇] ^{4–}
>12	Vanadate [VO ₄] ³⁻

Similar to the chromate containing LDH, the reported methods used to synthesize hydrotalcites with intercalated vanadium-based anions containing different pairs of divalent/trivalent cations in the brucite-like layers are co-precipitation, anion exchange, reconstruction, and hydrothermal method. Vanadium can be incorporated either in one of its anionic forms in the interlayer, mostly depending on the nature of the brucite-like cations and pH value (Table 4), or can be introduced as a cation, V(III) in the brucite-type layers (Table 5).

Suitable interlamellar distances are required to favor the intercalation of vanadates with similar hindrance. A good solution to increase the interlayer zone is to use proper-sized anions beforehand to swell the layers of the hydrotalcites, such as terephthalate or dodecyl sulphate. The size of the anions, as well as their charge density and orientation within the interlayer, has proven to have a considerable influence on the catalytic activity of the POM-LDH composites. Layered double hydroxides are known to be bifunctional catalysts, exhibiting neither purely acid nor basic character [18]. The Brønsted basicity of hydrotalcites is attributed to the existing surface hydroxyls and their combination with vanadium-based anions is believed to provide some Lewis acidity to the LDH. Polyoxometalates that are based on vanadium have often been applied in heterogeneous catalysis because of their interesting redox properties.

Decavanadate-intercalated LDH, having magnesium and aluminum as cations in the brucite-type layers, can be synthesized with great ease by direct ion exchange of a nitrate precursor with an aqueous NaVO₃ solution at an adequate acidic pH value with or without preswelling with terephthalate while following the method that was reported by Villa et al. [32]. The Raman data are particularly useful for distinguishing between intercalated species, such as $[VO_4]^{3-}$, $[V_2O_7]^{4-}$, $[V_4O_{12}]^{4-}$, and $[V_{10}O_{28}]^{6-}$ [33]. The Raman spectrum that was reported by Twu et al. of the LDH containing decavanadate, prepared by direct exchange of an LDH with an acidified V solution, indicates that decavanadate is the dominant anionic species found intercalated, as evidenced by the peaks at 320, 454, 534, 595, 834, 975, and 998 cm⁻¹ [34]. Although the signal to noise ratio of the spectrum for the LDH is not as good as that

for the $[V_{10}O_{28}]^{6-}$ ions in solution, it is quite clear that all of the characteristic peaks are attributed to decavanadate ions. For the sample that was heated to 160 °C, changes appear in both the XRD and Raman spectrum. These include a new reflection at 4.76 Å and the appearance of a broad band centered at 880 cm⁻¹ [34]. The characteristic Raman bands of the decavanadate are still present, as are the XRD reflections that are characteristic of the decavanadate-hydrotalcite complex. However, it was observed that the decavanadate species are transforming into other vanadate species at temperatures above 100 °C [34]. The XRD analysis of the decavanadate-LDH sample indicated a gallery height of 7.1 Å, which also suggested that the $[V_{10}O_{28}]^{6-}$ orientation with the C₂ axis is parallel to the layers [34]. The novel $[V_{10}O_{28}]^{6-}$ -MgAl-LDH composites are used as catalysts in a variety of electron transfer reactions.

Maciuca et al. [35] have successfully synthesized a solid containing decavanadate and pyrovanadate anions simultaneously intercalated between the brucite-type layers of a hydrotalcite. The UV-VIS spectrum of the sample exhibits a band at 300-320 nm, which is specific for V⁴⁺ having a pseudo-tetrahedral geometry, $[V_2O_7]^{4-}$ (representing 30% of V species), and a band around 420–450 nm, characteristic to V^{5+} ions with an octahedral arrangement, $[V_{10}O_{28}]^{6-}$ (70% of V species) [35]. The catalytic activity of the prepared LDH material was evaluated in the oxidation reaction of the tetrahydrothiophene to sulfolane with dilute H₂O₂ aqueous solution as oxidant. It was observed that low conversions were obtained for the vanadium-containing material, probably due to the formation of some complex species, other than $[V_{10}O_{28}]^{6-}$ or $[V_2O_7]^{4-}$, which probably do not possess any catalytic activity. Dobrea et al. [36] have also tried to intercalate decavanadate anions between the brucite-type layers of a MgAl-LDH. In the Raman spectra recorded, they have observed some bands in the regions 800–1000 cm⁻¹ and 200–370 cm⁻¹ that belong to two types of anions, namely $(VO_3)_n^{n-1}$ and $[V_{10}O_{28}]^{6-}$. The ratio between these anionic species strongly depends on the vanadium content in the LDH structure. When the V loading increases, the bands that are specific to the $(VO_3)_n^{n-1}$ ions decrease until complete disappearance, while the $[V_{10}O_{28}]^{6-}$ anions prevail [36]. Moreover, the XRD patterns of V-exchanged LDH samples display the same reflections characteristic to the layered materials, but at smaller values of 20. There are also some changes in the d_{003} -value that suggest the increase of the basal spacing and, thus, prove the replacement of smaller nitrate anions by larger species. At low concentrations of vanadate, only a partial exchange has occurred and reflections specific for both nitrate and oxyanions coexist in the XRD patterns. For higher V/Al ratios, the exchange was almost complete and the d₀₀₃-value increased up to 10.8 Å for V-LDH. The XRD patterns of the exchanged materials presented broader and lower intensity reflections when compared to the parent LDH accounting for the intercalation of various oxyanions species, which produce a certain level of disorder in the lamellar structure [36].

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	1	$[V_{10}O_{28}]^{6-}, [V_2O_7]^{4-}$	Anion exchange	Oxidation	Tetrahydrothiophene	4.6	[35]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Geraniol	90	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Nerol	95	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Perillyl alcohol	99	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Myrtenol	88	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Trans-Pinocarveol	79	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Isopulegol	76.1	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Nopol	54.9	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	β-Citronellol	13.7	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Verbenol	1.4	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Crotyl alcohol	65	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Cinnamyl alcohol	85	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	2-Cyclohexen-1-ol	21	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Epoxidation	Carveol	56.3	[32]
Mg,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Reconstruction	Alkoxylation	n-Butane	14.4	[37]
Mg,Al	1.5	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	Propane	25.7	[38]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	-	-	-	[34]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	-	-	-	[39]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Reconstruction	-	-	-	[39]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	Oxidation	Cyclohexene	23.2	[40]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	Propane	9.3	[41]
Mg,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	n-Butane	-	[42]
Mg,Al	2	$[V_{10}O_{28}]^{6-}, [VO_3]_n^{n-}$	Anion exchange	Oxidation	Dibenzothiophene	85.7	[36]
Mg,Al	2	$[V_2O_7]^{4-}$	Anion exchange	ODH	Propane	7.8	[38]
Mg,Al	2	$[V_2O_7]^{4-}$	Anion exchange	Oxidation	Cyclohexene	<1	[40]
Mg,Al	2.3;3.2;4.8	$[VO_4]^{3-}$	Co-precipitation	-	-	-	[43]
Mg,Al	2.5	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	-	-	-	[44]
Mg,Al	3	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	Propane	6.47	[45]
Mg,Al	3	[VO ₄] ^{3–} , CO ₃ ^{2–}	Co-precipitation	-	-	-	[46]
Mg,Al	3	$[VO_4]^{3-}$	Co-precipitation	-	-	-	[46]
Mg,Al	3	VO _x ⁻	Anion exchange	Anticorrosion	-	-	[47]

Table 4. Summary of LDH with intercalated vanadium-based anions.

Table 4. Cont.

Layer Cations	Layer Cations Molar Ratio Ir (M ^{II} :M ^{III})		Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	3	VO ²⁺	Anion exchange	-	-	-	[48]
Ni,Al	2.03	[V ₁₀ O ₂₈] ⁶⁻	Reconstruction	-	-	-	[49]
Ni,Al	2.31	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	-	-	-	[49]
Ni,Al	3	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	Propane	5.8	[50]
Cu,Cr	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	Alkoxylation	n-Butanol	53	[27]
Cu,Cr	2	$[V_2O_7]^{4-}$	Anion exchange	Alkoxylation	n-Butanol	30	[27]
Zn,Al	1	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	Oxidation	Cyclohexene	8.3	[40]
Zn,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	Oxidation	Cyclohexene	5.9	[40]
Zn,Al	2	[V ₁₀ O ₂₈] ⁶⁻	Co-precipitation	Anticorrosion	-	-	[51]
Zn,Al	2,3	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	ODH	Propane	6.1,6.5	[52]
Zn,Al	2	$[V_{10}O_{28}]^{6-}, [V_2O_7]^{4-}, [VO_3]_n^{n-}$	Anion exchange	-	-	-	[53]
Zn,Al	2	[V ₂ O ₇] ⁴⁻	Anion exchange	Anticorrosion	-	-	[54]
Zn,Al	2	[V ₂ O ₇] ⁴⁻	Anion exchange	-	-	-	[55]
Zn,Al	2	[V ₂ O ₇] ⁴⁻	Anion exchange	-	-	-	[56]
Zn,Al	2	VO _x -	Anion exchange	Anticorrosion	-	-	[47]
Zn,Al	3	$[V_{10}O_{28}]^{6-}, [V_2O_7]^{4-}, [VO_3]_n^{n-}$	Anion exchange	-	-	-	[53]
Zn,Al,Ce	0.29	[V ₂ O ₇] ⁴⁻	Anion exchange	-	-	-	[57]
Zn,Cr	1.75	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	-	-	-	[58]
Zn,Cr	2	[V ₁₀ O ₂₈] ⁶⁻	Anion exchange	Oxidation	Cyclohexene	2.9	[40]
Zn,Fe	2	[VO ₄] ³⁻	Hydrothermally	-	-	-	[59]

 Table 5. Summary of M^{II}M^{III}V-LDH.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al,V	3	CO3 ²⁻	Hydrothermally	-	-	-	[44]
Mg,Al,V	3	CO_{3}^{2-}	Hydrothermally	ODH	Propane	1.8	[41]

As previously reported [18], the overlapping and broadening of some reflections at higher 20 values can be attributed to the turbostratic effects that are caused by the new intercalated anionic species [36]. The samples that were prepared by Dobrea et al. were also tested as catalysts for the oxidation of dibenzothiophene (DBT) to dibenzothiophene-sulfone with H_2O_2 . It was observed that an increased amount of vanadium-based anions will produce a change of the oxyanion species from monomers (vanadate) to polymeric species (decavanadate). Moreover, the V-LDH samples suffered major modifications during the oxidation reaction, leading to a decreased catalytic activity that is attributed to their low stability [36].

Villa et al. have reported the obtaining of MgAl-layered double hydroxide pillared with vanadium under mildly acidic conditions, but this time the XRD, Raman, and IR characterization certified the presence in the interlayer region of pure decavanadate ($[V_{10}O_{28}]^{6-}$) anions [32]. The compound was used as a catalyst for the selective epoxidation of different allylic and homoallylic alcohols, mostly of terpene origin. The epoxidation of geraniol while using decavanadate-containing hydrotalcite (without or with preswelling) as catalyst, toluene as solvent, and t-BuOOH dissolved in decane as oxidant, led to high conversions of the substrate with minimal formation of geranial, which indicated that an increased effectiveness is obtained by working under anhydrous conditions that are able to prevent the decavanadate anions hydrolysis and stop any possible leaching. Additionally, it was demonstrated that low conversions and selectivities are obtained when vanadium-based anions are introduced in the LDH structure without rigorous pH control, which might lead to the formation of low-nuclearity polymers [32]. The decavanadate-containing LDH was used as catalyst for the epoxidation of various terpenic allylic alcohols in toluene with t-BuOOH/decane as an oxidant high conversions and epoxide selectivities being obtained for geraniol, nerol, perollyl alcohol, myrtenol, and trans-pinocarveol [32]. Even homoallylic alcohols (C=C–C–COH), such as isopulegol and nopol [32], were successfully epoxidized with high selectivity, but a decreased yield. Additionally, a rather low conversion and epoxide selectivity were obtained when β -citronellol was used as a substrate. A possible explanation for these unsatisfactory results can be attributed to the large distance between the alcohol group and the double bond. The allylic alcohols were smoothly epoxidized, except verbenol, whose bulky carbon skeleton did not allow for the coordination of the alcohol to the V [32]. High conversions with excellent selectivities were also obtained for crotyl alcohol and cinnamyl alcohol [32]. The results of the epoxidation strongly suggest that the allylic alcohol group of the substrate coordinates on the peroxo-V center [32] before oxygen transfer takes place. Therefore, it might be said that the active vanadium species participate in the epoxidation reaction with two coordination sites, one that is needed for the peroxide activation, and the other one for the alcohol coordination [32]. The vanadium atom is initially bound to the pillar with at least five V–O–V bonds [32], so it is mandatory to break one or two of these bonds to be reassured that the reaction takes place. However, there are still enough V–O–V bonds intact to keep all vanadium within the polyanions [32].

The alkoxylation of n-butanol with ethylene oxide (EO) to produce butoxy mono-ethylene glycol ether (BMGE) has been also studied on this type of LDH [37]. Malherbe et al. [37] used a commercial MgAl-LDH, which was reconstructed with intercalated decavanadate (sample MAV) after calcination, calcined at 450 °C (sample MAVCAL), and then rehydrated in water (MAVHYD) or in a 1 M KOH solution (MAVKOH). The calcination–rehydration procedure was used to observe the influence of rehydration on the reactivity of the mixed oxides. The XRD patterns of the three catalysts used in this study were also analyzed. The parent material used, a calcined hydrotalcite, presents the formation of a periclase MgO phase, while aluminum oxide could not be detected because of its amorphous structure. After the anion exchange and another calcination step, the periclase phase is significantly reduced [37]. A possible explanation is that a part of the magnesium participates in the formation of a ternary oxide (Mg–Al–V)–O [37]. The rehydration step decreases, even more, the proportion of the periclase phase in the final material and the XRPD patterns clearly indicate that most of the MgO phase will be transformed into an amorphous hydroxide form [37]. The catalytic performances of the new catalysts that were obtained after calcination or calcination–rehydration were tested in the synthesis of

2-butoxyethanol and compared to that of the untreated MAV. The conversion of ethylene oxide (EO) in a batch reactor increases with the reaction time in the order MAV < MAVHYD < MAVKOH [18]. The calcined solid, MAVCAL shows better conversion for low reaction times but it has the huge disadvantage of being deactivated after 20 h reaction. A likely cause of deactivation is associated to the appearance of a significant amount of a polymer type material in the product. The gelatinous solid is thought to contain polyethylene glycols (PEGs) and polyethoxylates, which strongly adsorb on the surface of the catalyst. A good solution is to rehydrate the calcined LDH in a KOH solution to eliminate the formation of unwanted polyethoxylates [37]. During rehydration, superficial O^{2-} sites are transformed into hydroxyl groups with lower basicity and high catalytic activity [37], while the use of KOH might either lead to an increase in the amount of OH groups or might ensure the formation of stronger ones.

Malherbe et al. [20] reported the synthesis of two systems, namely [CuCr–V₂O₇] and [CuCr–V₁₀O₂₈], which were also used as catalysts for the alkoxylation of n-butanol with ethylene oxide (EO) [20]. The parent material, [CuCr–Cl]-LDH was obtained by the co-precipitation method, and then through the appropriate *chimie douce* exchange reactions, the original chloride anions were replaced by decavanadate and pyrovanadate species [20]. From the catalytic tests, it was observed that higher conversions are obtained for the solid modified with decavanadate anions. The increased activity was attributed to a partial reduction of the vanadium species, with the active sites being not V^{5+} but V^{4+} [20].

The vanadate-exchanged layered double hydroxides with cations, such as Mg-Al [38,41,42,45], Ni-Al [50], or Zn-Al [52] in the brucite-like layers provide materials that differ in catalytic performance during the oxidative dehydrogenation (ODH) of various substrates (propane, n-butane), mostly depending on the nature of intercalated vanadate and the vanadium content [52], which can be modified during preparation. Consequently, the applied synthesis methods play a crucial role in the development of compounds with increased catalytic activities for ODH. The most active in the oxidative dehydrogenation of propane were the samples that were derived from the decavanadate-exchanged LDH under their calcined forms, namely their corresponding mixed oxides, while, for n-butane, the highest selectivity to ODH products and lowest selectivity to CO_x were observed for the V-poor solids [42]. These observations can be correlated with the increased nucleophilic character (basicity) of the oxygen atoms present in Mg–O–V units existing in orthovanadate than in V–O–V units (that lead to total oxidation) existing in α -Mg₂V₂O₇ and MgV₂O₆. At high vanadium loading, the presence of highly crystalline α -Mg₂V₂O₇ accounted for the observed decrease in 1,3-butadiene selectivity [42]. For ODH, acid and basic sites are both necessary for the reaction to take place, but it was proven that the total selectivity for dehydrogenated products was higher on the catalysts with increased base sites concentration [52].

Bahranowski et al. [40] have prepared different decavanadate-exchanged hydrotalcite-like compounds that were catalytically active in the selective oxidation of cyclohexene with dioxygen. Their activities mostly depended on the composition of the brucite layers, and decreased in the order MgAl > ZnAl > ZnCr [40]. The lowering of the M(II)/M(III) ratio in the brucite layer allowed for an increased loading of decavanadate anions, which eventually led to higher activity. Moreover, a pyrovanadate-exchanged-MgAl-LDH was also synthesized and used as a catalyst in the same reaction. It presented a lack of activity, which was probably due to the small interlayer distance that made the catalytic sites inaccessible. A considerable amount of epoxide was still observed in this case, which indicated the presence of decavanadate group in the interlamellar space [40]. Recently, Nejati et al. [59] obtained ZnFe–VO₄-LDH (Figure 7), which was used as an efficient electrocatalyst for water oxidation in alkali solution. In electrochemical water splitting, ZnFe–VO₄-LDH exhibits a superior OER performance, being expressed as lower onset overpotential, smaller Tafel slope, and larger exchange current density [59] when compared to the bare glassy carbon electrode. Layered double hydroxides that were intercalated with vanadium-based species were also used as anticorrosive materials. Tedim et al. [54] successfully reported the preparation of ZnAl–V₂O₇-LDH, which was able

to provide efficient active corrosion protection of an aluminum alloy. It was found that the inhibition by vanadates mainly occurs in alkaline solutions, where metavanadates and pyrovanadates are the most abundant. Vanadium can be introduced not only in the interlayer space, but also as a cation in the brucite-like layers (Table 5). Kooli et al. [44] obtained hydrotalcite-like materials containing vanadium, as V(III), together with Mg(II) and Al(III), in the layers, and carbonate in the interlayer. It was found that the nature of the precursor influences the type of the Mg-V-O phases formed; thus, when starting from $Mg_3(VO_4)_2$, the isolated $[VO_4]$ units are formed. Dula et al. [41] have tried to use this solid as a catalyst for oxidative dehydrogenation of propane (ODH), obtaining high conversions of the substrate, but with low selectivities.



Figure 7. Schematic structure of ZnFe–VO₄-LDH. Adapted from Ref. [59], Copyright 2018, Royal Society of Chemistry.

4.2.2. Molybdates

The intercalation of molybdenum-based anions in the structure of layered double hydroxides is a laborious process and it mostly depends on the pH and the Mo(VI) concentration. Moreover, the evolution of Mo(VI) in solutions is enriched, due to the existence of polymers that may lead to the obtaining of a variety of anions, the predominant ones being $[MoO_4]^{2-}$, $[HMoO_4]^{-}$, $[Mo_6O_{19}]^{2-}$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, and $[Mo_8O_{26}]^{2-}$ [60]. The geometry of smaller anions, such as $[MoO_4]^{2-}$, is tetrahedral, while larger anions, like $[Mo_6O_{19}]^{2-}$ and $[Mo_7O_{24}]^{6-}$, possess octahedral or distorted octahedral configuration. The intercalation of vanadates in the interlayer space of layered double hydroxides has been intensively studied, while that of molybdates has been restricted to the heptamolybdate $[Mo_7O_{24}]^{6-}$ ions that can be stabilized at a lower pH and can act as pillars that are used to expand the distance between the brucite-type sheets [61]. Additionally, Van Laar et al. [62] discovered that the $[MoO_4]^{2-}$ hydrolysis at a pH value of 10 inhibits the intercalation in the LDH structure and polymerization of molybdate does not occur until pH < 7 (Figure 8). The molybdate-containing LDH with slightly different chemical composition could be useful as selective catalysts for different processes. The first studies that were recorded for the characterization of oxomolybdate species at different acidic pH values were based on potentiometric titrations [63]. The main conclusion was that $[MoO_4]^{2-}$ ions are stable at pH 6.5, while the heptamolybdate $[Mo_7O_{24}]^{6-}$ exists in equilibrium with $[MoO_4]^{2-}$ at a pH between 4 and 6.5. Further acidification, 1.5 < pH < 2.9, enabled the obtaining of octamolybdate anion [Mo₈O₄₄]²⁻. Larger ionic aggregates are expected to appear at lower pH values, but there are no studies that are related to this statement [64]. Similar to the chromate- and vanadate-containing LDH, the

reported methods that are used to prepare hydrotalcites with intercalated molybdenum-based anions containing different pairs of divalent/trivalent cations in the brucite-like layers are co-precipitation, anion exchange, and hydrothermal method. The studies showed that molybdenum can be introduced either as one of its anionic forms in the interlayer (Table 6) or as a cation in the brucite-type layers (Table 7).



Figure 8. The polymerization degree of oxomolybdate versus pH. Adapted from Ref. [65], Copyright 2004, American Chemical Society.

The most used method for molybdate incorporation in MgAl-LDH structure is the anionic exchange. However, Drezdon et al. [66] reported a new technique derived from the classical ionic exchange that primarily involves the synthesis of an organic anion-pillared precursor, also called swelling agent, which is subsequently exchanged with an adequate polyoxometalate anion under acidic conditions [66]. In this case, the organic anion needs to have slightly larger dimensions than the polyoxometalate to be incorporated. By creating an acidic medium, the organic anion already incorporated in the LDH will be protonated, which weakens the electrostatic interaction between the cationic layers and the intercalated organic species and, thus, allowing for the partial exchange of the organically-pillared hydrotalcite with the polyoxometalate [66]. Moreover, the anion affinity in LDH interlayers depends on the size of the ion and its charge [67]. The monovalent anions have lower affinities and, hence, their participation in anion exchange reactions is favored when compared to divalent anions [67]. Based on the XRD results, Davantes et al. [68] were able to create a representative scheme that describes the interlayer exchange of different anions (Figure 9). The affinity series decreases in the order $[Mo_7O_{24}]^{6-} > CO_3^{2-} > [MoO_4]^{2-} > SO_4^{2-}$ [60]. The diffraction patterns of the Mo-intercalated samples that were obtained by Carriazo et al. [69] are characteristic to hydrotalcite-like structure, indicating a rhombohedral packing of the layers. The powder XRD patterns of layered double hydroxides usually present a decrease in the intensities of the (001) lines, while the value of lincreases, but, in this situation, it was observed that the intensity of the (006) and (009) lines are larger than that of the (003) line.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	1	[Mo4 ^V Mo8 ^{VI} O40] ⁷⁻	Anion exchange	Epoxidation	Cyclohexene	<1	[70]
Mg,Al	1.46	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Dibenzothiophene	94	[71]
Mg,Al	1.46	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Anthracene	18.7	[71]
Mg,Al	1.5	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Norbornadiene	49.6	[72]
Mg,Al	1.5	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Benzonorbornadiene	76.1	[72]
Mg,Al	1.5	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Cyclohexene	55.4	[72]
Mg,Al	1.59	[Mo ₇ O ₂₄] ⁶⁻	Hydrothermal	Oxidation	Dibenzothiophene	98	[71]
Mg,Al	1.59	[Mo ₇ O ₂₄] ⁶⁻	Hydrothermal	Oxidation	Anthracene	52.4	[71]
Mg,Al	1.5	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	30	[73]
Mg,Al	1.6	[Mo ₇ O ₂₄] ⁶⁻	Co-precipitation	Oxidation	tert-Butanethiol	30	[74]
Mg,Al	1.6	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Tetrahydrothiophene	76.4	[35]
Mg,Al	2	$[Mo_2O_7]^{2-}$	Anion exchange	Dehydrogenation	Propane	<30	[75]
Mg,Al	2	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Dehydrogenation	Propane	<30	[75]
Mg,Al	2	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	-	-	-	[69]
Mg,Al	2	[Mo ₇ O ₂₄] ⁶⁻	In situ hydrolysis	Epoxidation	Cyclohexene	<1	[68]
Mg,Al	2	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Dibenzothiophene	90	[36]
Mg,Al	2	$[MoO_4]^{2-}$	Anion exchange	Dehydrogenation	Propane	<30	[75]
Mg,Al	2	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	33	[73]
Mg,Al	2	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	>95	[76]
Mg,Al	2	[MoO ₄] ²⁻	Co-precipitation	Condensation	Adamantanone	94	[77]
Mg,Al	2	[MoO ₄] ²⁻	Co-precipitation	Anticorrosion	-	-	[78]
Mg,Al	2;3;4	$[MoO_4]^{2-}$	Co-precipitation	-	-	-	[43]
Mg,Al	2.25	[MoO ₄] ²⁻ , NO ₃ ⁻ , CO ₃ ²⁻	Co-precipitation	Oxidation	Cyclohexene	13.9	[79]
Mg,Al	2.3;4;9	$[MoO_4]^{2-}$	Anion exchange	Oxidation	1-Methyl-1-Cyclohexene	11;12;19	[62]
Mg,Al	2.3	[MoO ₄] ^{2–} 12.5%, pTOS 87.5%	Anion exchange	Oxidation	1-Methyl-1-Cyclohexene	22	[62]
Mg,Al	2.3	[MoO ₄] ²⁻ 25%, pTOS 75%	Anion exchange	Oxidation	1-Methyl-1-Cyclohexene	21.5	[62]
Mg,Al	2.45	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	34	[73]
Mg,Al	2.5	[Mo ₇ O ₂₄] ^{6–} , pTOS, CO ₃ ^{2–}	Anion exchange	Oxidation	Cyclohexene	16.7	[79]
Mg,Al	2.64	$[MoO_{4}]^{2-}$	Co-precipitation	Oxidation	tert-Butanethiol	75	[74]
Mg,Al	2.7	[MoO ₄] ^{2–} , NO _{3–} , CO ₃ ^{2–}	Co-precipitation	Oxidation	Cyclohexene	12.5	[79]
Mg,Al	2.7	[MoO ₄] ^{2–} , pTOS, CO ₃ ^{2–}	Anion exchange	Oxidation	Cyclohexene	15.3	[79]
Mg,Al	2.75	$[MoO_4]^{2-}$	Anion exchange	Oxidation	tert-Butanethiol	80	[74]
Mg,Al	2.75	$[MoO_4]^{2-}, CO_3^{2-}$	Anion exchange	Oxidation	Cyclohexene	12.5	[79]

Table 6. Summary of LDH with intercalated molybdenum-based anions.

Table 6. Cont.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	3	[MoO ₄] ²⁻	Anion exchange	Halodecarboxylation	Cinnamic acid	80	[80]
Mg,Al	3	$[MoO_4]^{2-}$	Co-precipitation	-	-	-	[81]
Mg,Al	3	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	35	[73]
Mg,Al	3	$[MoO_4]^{2-}$	Co-precipitation	Oxidation	Cyclohexene	14.4	[79]
Mg,Al	3	$[MoO_4]^{2-}$	Co-precipitation	-	-	-	[67,82]
Mg,Al	3	[MoO ₄] ²⁻	Anion exchange	-	-	-	[83]
Mg,Al	3	[MoO ₄] ²⁻ , CO ₃ ²⁻	Anion exchange	Oxidation	Cyclohexene	13.1	[79]
Mg,Al	3	$[MoO_4]^{2-}, NO_3^{-}$	Co-precipitation	Oxidation	Cyclohexene	13.3	[79]
Mg,Al	3	[MoO ₄] ^{2–} , pTOS	Anion exchange	Oxidation	Cyclohexene	15.9	[79]
Mg,Al	3	[Mo ₇ O ₂₄] ⁶⁻ , pTOS	Anion exchange	Oxidation	Cyclohexene	17.5	[79]
Mg,Al	4	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	35	[73]
Mg,Al	5	$[MoO_4]^{2-}$	Anion exchange	Peroxidation	β-Citronellol	-	[73]
Ni,Fe	9	[MoO ₄] ²⁻	Hydrothermal	OER	Water	-	[84]
Ni,Zn	1.5	[MoO ₄] ²⁻	Anion exchange	Transesterification	Soybean oil	20	[85]
Ni,Al	2.1	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Norbornadiene	83.1	[72]
Ni,Al	2.1	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Benzonorbornadiene	100	[72]
Ni,Al	2.1	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Cyclohexene	81	[72]
Zn,Al	1	[Mo4 ^V Mo8 ^{VI} O40] ⁷⁻	Anion exchange	Epoxidation	Cyclohexene	<1	[70]
Zn,Al	1	PM0 ₁₂ O ₄₀ ³⁻	Anion exchange	Esterification	Acetic acid	77.2	[86]
Zn,Al	1.56	$[MoO_4]^{2-}$	Co-precipitation	Anticorrosion	-	-	[87]
Zn,Al	1.9	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Norbornadiene	64.5	[72]
Zn,Al	1.9	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Benzonorbornadiene	100	[72]
Zn,Al	1.9	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Cyclohexene	77.27	[72]
Zn,Al	2	$[MoO_4]^{2-}$	Anion exchange	Anticorrosion	-	-	[88]
Zn,Al	2	[Mo ₇ O ₂₄] ⁶⁻	Co-precipitation	Epoxidation	Cyclohexene	<1	[68]
Zn,Al	2	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange		-	-	[69]
Zn,Al	2.06	[Mo ₇ O ₂₄] ⁶⁻	Anion exchange	-	-	-	[60]
Zn,Al	2.1	$[MoO_4]^{2-}$	Chimie douce	-	-	-	[89]

 Table 7. Summary of MMo-LDH (M-metal).

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Co,Mo	3	CO3 ²⁻	Co-precipitation	Adsorbent	-	-	[90–92]
Zn,Mo	2.3;4;9	CO ₃ ^{2–}	Co-precipitation	-	-	-	[93]



Figure 9. Schematic representation of molybdate exchange in LDH. Adapted from Ref. [60], Copyright 2013, American Chemical Society.

This abnormal behavior is specific for LDH intercalated with different POM and it appears to be due to the large atomic scattering factor of the interlamellar species [69]. The ZnAl-LDH containing heptamolybdate in the interlayer presents sharp and very symmetric lines probably due to its ordered packing of the layers. Additionally, the value of the interlayer distance was similar to the height of the heptamolybdate (7.2 Å) with its C₂ axis being perpendicular to the layers. This orientation favors the formation of a strong interaction between the brucite-like layers and the intercalated anion [69]. For the samples MgAl–Mo and NiAl–Mo, a broad reflection that is close to 11 Å is observed, which suggests the presence of a low-ordered phase of Mg-POM [94] or a novel phase with the anion grafted to the hydroxyl layer [69]. Raman studies [95] indicated that this is due to a small amount of $[MoO_4]^{2-}$ anions that resulted from the polyanion hydrolysis [69]. Dobrea et al. [36] have also tried to intercalate molybdenum-based anions between the brucite-type layers of a MgAl-LDH with different Mg/Al ratios. In the Raman spectra that were recorded for the Mo-LDH samples, it was observed that the most important bands are present in the regions 890–950 and 300–360 cm⁻¹, and they are most likely attributed to the main types of molybdenum-based anions that can appear within the hydrotalcite structure: $[MoO_4]^{2-}$, $[Mo_2O_7]^{2-}$, and $[Mo_7O_24]^{6-}$ [36].

At low Mo loading, the Raman spectra display bands at about 895 and 320 cm⁻¹, which clearly belong to the monomer $[MoO_4]^{2-}$ species. In these spectra, there are also some bands at 1050 and 709 cm⁻¹ that are probably attributed to the residual NO₃⁻ anions [36]. By increasing the Mo loading, a more complex Raman spectra was obtained, due to the formation of octahedrally coordinated polymolybdate species (i.e., $[Mo_2O_7]^{2-}$ with band at 920 cm⁻¹ and $[Mo_7O_{24}]^{6-}$ with bands at 947 and 358 cm⁻¹), while the bands characteristic for the nitrate and molybdate ions decreased in intensity until their complete disappearance. The sample with the highest Mo concentration mainly contained heptamolybdate anions [36]. It can be stated that different oxyanions are inserted in the structure of hydrotalcites after anion exchange, and their nature mostly depended on the molybdate species loading and, of course, on the pH used by analyzing the wavenumbers that are specific for various Mo species found in literature (Table 8) and the Raman spectra of the compounds that were prepared by Dobrea et al. [36]. Infrared spectroscopy appears to be a better technique for analyzing the structure of Mo(VI) species, but only in aqueous solutions, not necessary intercalated within the hydrotalcite materials, even though the Raman measurements have been widely used for the characterization of polymolybdate anions intercalated between the cationic layers of LDH.

Table 8. Raman frequencies (cm⁻¹) for Mo oxyanions species. Data taken from Refs. [12,36,71].

Vibration Tuna *	Anion Species						
vibration type	[MoO4] ²⁻	[Mo ₂ O _{7]} ²⁻	[Mo ₇ O ₂₄] ⁶⁻	$[Mo_8O_{26}]^{4-}$			
υ _s (Mo=O)	895-898	920–930	937–0945	965			
vas (Mo=O)	837-846	-	903	925			
δ (Mo=O)	300-320	355	355-365	370			
υ (Mo-O-Mo)	-	-	564	860			

* v_s = symmetric stretching mode attributed to Mo=O bond vibrations; v_{as} = antisymmetric stretching mode; δ = bending mode.

However, Yu et al. [88] were able to record the FT-IR spectrum of $[MoO_4]^{2-}$ -pillared ZnAl hydrotalcite, which consists of bands attributed to hydroxyl stretching vibrations (3430 cm⁻¹) and bending modes of interlayer water (1630 cm⁻¹). There is also a band at 1368 cm⁻¹ that is specific for CO_3^{2-} stretching mode that might indicate the contamination of the material by atmospheric CO_2 [88]. The band corresponding to the antisymmetric mode of Mo–O–Mo in $[MoO_4]^{2-}$ is observed at 834 cm⁻¹. Moreover, the bands at 620, 559, and 428 cm⁻¹ can be related to the vibrations modes of the oxygen atoms at the layer crystal lattice [88]. Polyoxometalates that are based on molybdenum have been often applied in heterogeneous catalysis due to their interesting redox properties.

Layered double hydroxides containing heptamolybdate $[Mo_7O_{24}]^{6-}$ anions in the interlamellar space that were prepared by anion exchange starting from suitable precursors proved to be effective catalysts in the epoxidation of different substrates.

Carriazo et al. [72] have prepared, by the ion exchange method, starting from suitable precursors containing terephthalate, three different LDH, combining Al with different divalent cations (Mg, Zn, and Ni) to obtain the brucite-like layers and heptamolybdate in the interlayer [72]. The compounds were further used as catalysts for the epoxidation of norbornadiene, benzonorbornadiene, and cyclohexene. The hydrotalcite composition and the reaction solvents, i.e. hydrogen peroxide, dioxane, or dioxane–butyl maleate influenced the selectivity to epoxides [72]. For the hydrotalcites containing NiAl–Mo and ZnAl–Mo, the selectivity in epoxide was very good, approximately 85% for norbornadiene and almost 100% for benzonorbornadiene [72]. When cyclohexene was used as a substrate, the same tendency as in previously mentioned cases was observed: NiAl–Mo and ZnAl–Mo catalysts led to the highest selectivities in epoxide. As for the solvent, the best results were obtained while using dioxane or acetone. The differences between these two solvents were quite small. However, the replacement of dioxane with dioxane–butyl maleate mixture led to a decrease in the selectivity to epoxide [72].

Cyclohexene was also used as a substrate for the epoxidation reaction in the work that was reported by Sels et al. [70]. The catalysts, in this case, were two hydrotalcites containing MgAl or ZnAl as cations in the layers. Both LDH were obtained by co-precipitation and intercalated by the anion exchange method with molybdenum blue, a mixed-valency isopolyacid containing Mo^V and Mo^{VI}, namely $[Mo_4^V Mo_8^{VI} O_{40}]^{7-}$ [70]. The exchange within the LDH is rapid because of its high negative charge. However, it was observed that the nature of the cations from the brucite-type layers of the LDH considerably influenced the long-term stability of Mo blue. With Mo blue on MgAl-LDH, the material has changed its color from deep blue to colorless within a few weeks [70]. This indicates that Mo blue, which is synthesized in a solution at pH 3, is decomposed in time at the surface of MgAl-LDH, which has pronounced basic properties [70]. Such decomposition problems do not appear with Mo blue that is exchanged on ZnAl-LDH or on DS-ZnAl-LDH (ZnAl-LDH pre-exchanged with dodecyl sulfate) [70]. The results on epoxidation of cyclohexene with H_2O_2 and with Mo blue exchanged on MgAl-LDH as catalyst indicate a low olefin conversion. Before the addition of H2O2 in the reaction medium, the catalyst presents the yellow shade that is specific to the Mo^{VI} form of the isopolyacid [70]. The color changed rapidly into red, suggesting the presence of tetraperoxomolybdate $[Mo(O_2)_4]^{2-}$ indicating the isopolyacid structure destruction [70]. A slightly higher olefin conversion is obtained with Mo blue that is exchanged on ZnAl-LDH.

Gardner et al. [68] have also prepared two catalysts that are derived from Mg₂Al and Zn₂Al layered double hydroxides intercalated by heptamolybdate species and then used them for epoxidation of cyclohexene. The catalysts were synthesized by different methods, in situ hydrolysis in the case of Mg₂Al-LDH and anion exchange for the material containing Zn. In the epoxidation reaction, it was observed that all of the heptametallate-intercalated LDH are not stable under the reaction conditions being converted into lower nuclearity species, which migrate to the LDH surface and lead to low conversions and selectivities [68].

Zavoianu et al. [79] have studied the effect of the synthesis methods on the physicochemical properties and catalytic performance of MgAl-molybdate-LDH in cyclohexene oxidation with hydrogen peroxide [79]. Five samples have been prepared by (i) ionic exchange procedure, as described

by Kwon et al. [63], between a hydrotalcite containing carbonate anions previously obtained by co-precipitation at pH = 10 and low supersaturation with aqueous Na₂MoO₄; (ii) competitive ionic exchange at pH 10 while using a hydrotalcite containing carbonate anions, aqueous Na₂MoO₄, and p-toluene sulfonic acid (pTOS) as swelling agent, based on Van Laar studies [62]; (iii) exchange of the carbonate precursor LDH with pTOS at pH 4.5, followed by the exchange with molybdate at pH 4.5 under a constant stirring for 24 h and a readjustment of the pH to 10 using NaOH; (iv) direct synthesis at high supersaturation and pH 10 [18]; and, (v) direct synthesis at low supersaturation and pH 10 [18,79]. The characterization techniques used (FTIR, Raman, and UV–Vis spectroscopies) indicate the presence of $[MoO_4]^{2-}$ and smaller amounts of $[Mo_7O_{24}]^{6-}$ species in all of the samples. The catalytic activity of the solids is correlated with the basicity, which decreases with the increase in Mo loading [18,79]. The samples containing a low Mo amount (about 2.5–2.8%) in the form of $[MoO_4]^{2-}$ in the interlayer and increased magnesium concentration in the brucite layers have proven to favor the hydroperoxidation reaction of cyclohexene, while the catalysts also containing $[Mo_7O_{24}]^{6-}$ species in their structure encouraged the appearance of epoxides [79].

Van Laar et al. [62] reported a molybdate-exchanged layered double hydroxide heterogeneous catalyst for the conversion of H_2O_2 into singlet molecular dioxygen (1O_2). The distinction between epoxidation and ¹O₂ oxygenation was studied by using 1-methyl-1-cyclohexene as a substrate. The highest product yield at complete H₂O₂ consumption was obtained by the LDH catalyst containing less Mo amount [62]. Whalen et al. [73] have also studied the disproportionation of H_2O_2 into singlet oxygen by using molybdate-exchanged MgAl-LDH with Mg/Al ratio between 1.5 and 5. The chemical trapping (CT) of ${}^{1}O_{2}$ with β -citronellol performed the production of singlet oxygen. The efficiency of H_2O_2 has been enhanced with the increase of Mg/Al ratio. The yield of the generated 1O_2 was around 30-35%. The rate of H_2O_2 disproportionation sharply decreases when the Mo loading is increased due to the high Mo amount, which reduces the access of β -citronellol to the [MoO₄]²⁻ anions in the interlayer space, leading to the loss of a part of the ¹O₂ produced within the LDH. A few years later, Whalen et al. [76] discovered a way of increasing the oxidant efficiency of molybdate-containing MgAl-LDHs, which consists in pretreating the catalyst with 1,3-propanediol, glycerol, ethylene glycol, or 1,2-propanediol [76]. The peroxidation of different olefins with this glycol-modified catalyst led to conversions above 88% and selectivities up to 99% [76]. Mild oxidation of tetrahydrothiophene (THT) to sulfolane has been studied on molybdenum-containing LDH that was obtained by anionic exchange of a nitrate-LDH precursor with an aqueous solution of Na₂MoO₄·2H₂O at pH 4.5 by Hulea et al. [35]. The oxidation of tetrahydrothiophene was highly selective towards the sulfoxidation reaction, exclusively resulting in sulfoxide and sulfolane. A conversion of 98% was reached after 45 min. reaction, with a selectivity to sulfolane of 78%.

Ciocan et al. [71] have synthesized two series of Mo-containing hydrotalcites by different techniques: (i) anion exchange at atmospheric pressure, after complete synthesis of LDH, and (ii) anion exchange under hydrothermal conditions during the aging step of LDH synthesis. The influence of the preparation technique on the catalytic properties was investigated in the oxidation of dibenzothiophene (DBT) and anthracene with hydrogen peroxide [71]. The catalytic tests that were performed under moderate conditions (40–70 °C) indicated that both types of catalysts are efficient, but the solids that were prepared under hydrothermal conditions are more active, probably due to their larger specific surface area, which makes the access to active sites easier [71]. Dobrea et al. studied the oxidation of dibenzothiophene with H₂O₂ while using as catalyst a MgAl-LDH intercalated with heptamolybdate species [45]. The catalyst was characterized by Raman spectroscopy before and after the reaction to verify the stability. The DBT conversion strongly increased with the metal content in the Mo-LDH [45], which was obviously due to the increase in the number of active sites. Large polyoxymolybdate species were formed at high metal loadings, leading to an important increase in the distance between the LDH layers and, hence, to increased accessibility of the large DBT molecule to the catalytic centers [45]. The Raman spectra recorded confirmed the increased stability of Mo-oxoanions contained in layered double hydroxides, in contrast with the V-oxoanions [45].

Zavoianu at al. [74] have studied the oxidation of tert-butanethiol (t-BuSH) while using as catalysts Mo-LDH samples that were obtained from two different molybdenum sources, e.g. Na₂MoO₄ or (NH₄)₆Mo₇O₂₄ and prepared by two methods: (i) ionic exchange and (ii) co-precipitation at pH 10 under high supersaturation [74]. When Na₂MoO₄ was used as a molybdenum source, crystalline materials with relatively high basicity and fine dispersion of molybdate species were obtained. These samples showed the best catalytic activities, leading to high conversions of t-BuSH of about 80%. By changing the molybdenum source to (NH₄)₆Mo₇O₂₄, solids with a lower crystallinity, smaller surface area, lower basicity, and catalytic activity were obtained [88]. Mitchell and Wass [75] have synthesized the Mo-LDH catalysts while applying different preparation methods based on the anion exchange technique to be used in propane ODH. The most active and selective catalyst in this reaction was that prepared by classical anion exchange between a calcined commercial hydrotalcite and ammonium dimolybdate with prior impregnation with terephthalic acid and pH adjusted to 4.5 with nitric acid [18,75].

Choudary et al. [80] have reported the use of molybdate-containing MgAl-LDH catalyst for the synthesis of β -bromostyrenes in aqueous medium via the halodecarboxylation reaction of cinnamic acid. The high catalytic activity of the LDH system was attributed to its basic character and the large positive charge of brucite layers which may further lead to the enrichment of bromide ion near the solid surface [80]. Moreover, the excess of positive charge on the LDH surface shields the negative charge of the peroxomolybdate and bromide, ensuring high halide oxidation rates in this way [80]. Das and Parida [86] reported a parallel study of the esterification of acetic acid with n-butanol on ZnAl-LDH intercalated with tungstophosphoric (TPA) and molybdophosphoric (MPA) acid. The conversion of acetic acid was higher for the solid that was prepared with MPA (84.15%), although the selectivity to the ester was 100% for both of the samples. This behavior might be ascribed to the increased surface Brønsted acidity and the specific surface area shown by the Mo-containing sample [18,86]. Colombo et al. [85] prepared at two different pH values a NiZn LDH initially intercalated with acetate ions, which were subsequently replaced with molybdate anions via an ion exchange reaction. The basal spacing in the NiZn-LDH decreased from 13.08 Å to ca. 9.5 Å regardless of the working pH, [85], which might suggest the intercalation of hydrated molybdate anions. The as-synthesized material and the solid that was obtained by thermal treatment at 250 °C (basal spacing reduced to 7.35 Å due to dehydration) were tested as catalysts for the methyl transesterification of soybean oil [85]. All of the materials were catalytically active and led to high conversions of the substrate, but poor selectivities [85].

Klemkaite-Ramanauske et al. [77] prepared molybdate-containing MgAl layered double hydroxides by using different variations of the co-precipitation method and used them as catalysts for the synthesis of 2-adamantylidene(phenyl)amine Schiff base. All of the synthesized molybdate-containing layered double hydroxides presented similar catalytic activity for the studied reaction, no matter what co-precipitation route was used for preparation [77]. LDH is usually prepared from divalent and trivalent cations, but Mostafa et al. [90–92] succeeded to synthesize by co-precipitation method while using ammonium hydroxide and ammonium carbonate as precipitating agents, a highly crystalline CoMo-LDH, as a new type of M²⁺M⁶⁺-LDH. This new type of LDH had shown a highly energetic surface due to the formation of +4 charges between Co²⁺ and Mo⁶⁺, as identified by XPS analysis. Muramatsu et al. were also successful in the preparation of a ZnMo-LDH belonging to this new generation of hydrotalcites.

Apart from the crucial role in the conventional catalysis, Mo-containing LDH can also be used as photocatalyst for electrocatalytic water oxidation [84], as adsorbent [60,69,89], or as an anti-corrosion material [78,88].

4.3. Layered Double Hydroxides Intercalated with High-Nuclearity Oxometalates: Iso and Hetero-Polyoxometalates

Polyoxotungstates (POW) are a large family of metal-oxo anionic clusters that have a variety of structures with a definite size and shape and a wide range of applications [96,97]. The preparation of tungstate-based anions intercalated within the hydrotalcite-like structure is a difficult task, as these materials are usually unstable under basic conditions and the synthesis process is strongly dependent on pH and other reaction conditions (temperature, contact time between the LDH and POM, etc.) [65]. Polyoxotungstates that are incorporated into the interlayer of layered double hydroxides present different structures: Keggin, Dawson, or Finke type [65]. Each type of POW can impose a particular gallery pore structure upon pillaring reaction, which results in new members of the class of LDH-POW derivatives. Figure 10 summarizes the pH ranges that correspond to the stability of the different W-POM.



Figure 10. pH ranges corresponding to the stability of different polyoxotungstates. Adapted from Ref. [65], Copyright 2004, American Chemical Society.

Having a nearly spherical shape due to its tetrahedral symmetry, the α -Keggin ion [α -H₂W₁₂O₄₀]^{6–} will limit the possible gallery heights upon intercalation in LDH structure [97]. Moreover, this particular Keggin structure presents a diameter of approximately 10 Å, which is two-times larger than the brucite-like layer thickness (ca. 4.8 Å). However, LDH materials intercalated with larger POW than Keggin ions are more interesting, due to the increased access to the interlayer space [97]. The other two POW with lower molecular symmetries, as seen in Figure 11, can lead to gallery micropores of different sizes, depending on their interlayer orientations [97]. For example, the parallel and perpendicular gallery orientations of [α -P₂W₁₈O₆₂]^{6–} having the D_{3h} symmetry attributed to the Dawson structure, and of Co₄(H₂O)₂(PW₉O₃₄)^{10–} with the C_{2h} symmetry specific for the Finke structure, can result in 2.1 and 5.0 Å differences, respectively, in the pore size [97]. The reported methods used to prepare hydrotalcites with intercalated tungsten-based anions containing different pairs of divalent/trivalent cations in the brucite-like layers are anion exchange, co-precipitation, and reconstruction, similar to the chromate-, vanadate-, and molybdate-containing LDH (Figure 12). Table 9 summarizes all of the reported studies.



Figure 11. Schematic representation of LDH pillared by Keggin POW ions with nearly spherical symmetry and by Dawson and Finke POW ions with cylindrical symmetry. Adapted from Ref. [97], Copyright 1996, American Chemical Society.



Figure 12. Representative methods used to prepare POW-LDH: (I) co-precipitation; (II) anion exchange; (III) anion exchange with calcined metal oxide; IV and VI, organic precursor methods, consisting in adding a preswelling agent; (V) anion exchange between an aqueous synthetic meixnerite and a POW solution. Adapted from Ref. [97], Copyright 1996, American Chemical Society.

The acid-base interaction that exists between POW anions (hydrolytically unstable at weakly acid to basic pH) and LDH (with a basic character) induces a partial dissolution of the brucite-like layers influencing the final cation ratio, also leading to the formation of another phase, probably a Mg-rich salt of the POW that deposits on the surface of LDH. Therefore, special attention must be given to the method that is used to synthesize POW-LDH and the working conditions. Choudary at al. [98] have reported the obtaining of a tungstate-intercalated LDH, which was further used as biomimetic catalyst for mild oxidative bromination and bromide-assisted epoxidation reactions of different aromatic and olefinic substrates. While taking that conventional bromination reactions typically use elemental bromine, a pollutant and health hazard, into consideration, this study is also important from environmental point of view [18]. The NiAl-LDH-WO₄²⁻ catalyst prepared enabled the electrophilic bromination of the substrates in mild and well-controlled conditions. The majority of the reactions presented a high selectivity of halonium ions with complete stereoselectivity [98]. The methoxybromination of some aliphatic olefins showed moderate chemoselectivity due to the formation of a considerable amount of dibromides, while, in all other cases, e.g. in the methoxybromination of aromatic olefins, or in the bromohydroxylation of aromatic or aliphatic olefins, chemo-, regio-, and stereoselectivity were high [98]. Suitable substrates for bromide-assisted epoxidation have proven to be geminally di-, tri-, and tetra-substituted olefins. Additionally, the reaction can be easily switched from bromohydroxylation to epoxidation by changing the solvent [98]. The bromide-assisted epoxidation shows much higher turnover frequencies than classical W-catalyzed epoxidations [98].

Jacobs et al. [99] have also used MAI–Cl-LDH (M = Mg, Ni) exchanged with tungstate as catalysts for mild oxidative bromination. The XRD data of the prepared compounds did not show any swelling upon exchange, despite Raman spectroscopy indicating the typical features of tetrahedral $[WO_4]^{2-}$ units, which suggested that $[WO_4]^{2-}$ should be mainly located in edge positions. Moreover, the solids were recycled after each bromination reaction and then reused in the same chemical transformation maintaining their oxidative stability and unaffected catalytic activity [99]. The prepared catalyst allowed for the electrophilic bromination of a wide range of nucleophilic substrates (olefins, 1,3-diketones, aromatics) with high selectivity under mild conditions [99]. Choudary et al. [100] have prepared by anion exchange two MgAI-LDH intercalated with $[WO_4]^{2-}$ and $PO_4[WO(O_2)]_4$, respectively, and used them as catalysts for the oxidation of thioanisole with H_2O_2 . The LDH-WO₄ exhibited the highest turnover frequency of 21.7 h⁻¹ when compared to the other LDH catalyst.

Usually, when a reaction that is catalyzed by POM–LDH solids occurs inside the interlamellar region, a decrease in hydrophobicity would lead to an intensified diffusion of the substrate and/or the final products [18]. Following this statment, Palomeque et al. [101] have studied the epoxidation of cyclohexene with MgAl-hydrotalcite-intercalated organotungstic complexes that were synthesized by different methods. The tungsten-based anions were incorporated within the LDH structure either by anionic exchange or by complexation with phosphonic acids previously incorporated between the sheets [101]. Phenyl-/dodecylphosphonic acids and peroxotungstic salts were intercalated into the LDH and they led to the expansion of the lamellar lattice and the complexation of phosphonic acids with W-peroxo species [101]. These catalysts were tested in the epoxidation of cyclohexene with hydrogen peroxide or tertbutyl hydroperoxide as oxidants. The materials that were prepared by anionic exchange only gave epoxycyclohexane, but with moderate yields, whereas those that were prepared from previously incorporated phosphonic acids gave high selectivities (50–72%) towards allylic oxidation products [101]. The efficiency of the phosphonato-peroxotungstatic species is the result of the intrinsic reactivity of the WO₅–O=P subunit [101]. Carriazo et al. [102] have synthesized polyoxometalates $[H_2W_{12}O_{40}]^{6-}$ and $[W_4Nb_2O_{19}]^{4-}$ intercalated between the brucite-like layers of MgAl and ZnAl hydrotalcites by anion exchange, starting from the corresponding nitrate LDH precursors. The samples were also tested in the epoxidation reaction as in the previous case, but the substrate was cyclooctene and the oxidants were H_2O_2 or t-BuOOH, this time. The results showed that both of the anions are effectively located in the interlayer space, maintaining their pristine structures without depolymerization [102].

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	1	[WO ₄] ²⁻	Anion exchange	Mild oxidative bromination	Olefins	84	[99]
Mg,Al	1	$[WO_4]^{2-}$	Anion exchange	Mild oxidative bromination	Olefins	61;89	[99]
Mg,Al	1	[WO ₄] ^{2–}	Anion exchange	Oxidation	Thioanisole	94	[100]
Mg,Al	1	$PO_4[WO(O_2)]_4$	Anion exchange	Oxidation	Thioanisole	90	[100]
Mg,Al	1	$C_6H_5PO_3(WO_5)_2$	Anion exchange	Epoxidation	Cyclohexene	12.4	[101]
Mg,Al	1.92	[CoW ₁₂ O ₄₀] ⁵⁻	Anion exchange	Oxidation	Benzaldehyde	98.8	[103]
Mg,Al	1.99	[WO ₄] ²⁻ ,[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Benzothiophene	60	[35]
Mg,Al	1.99	$[WO_4]^{2-}, [W_7O_{24}]^{6-}$	Anion exchange	Oxidation	Dibenzothiophene	80	[35]
Mg,Al	1.99	[WO ₄] ²⁻ ,[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Diphenyl sulfide	90	[35]
Mg,Al	1.99	[WO ₄] ²⁻ ,[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Benzyl-phenyl sulfide	100	[35]
Mg,Al	1.99	[WO ₄] ²⁻ ,[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Methyl-phenyl sulfide	100	[35]
Mg,Al	2	[W ₇ O ₂₄] ⁶⁻	Anion exchange	Photodegradation	Hexachlorocyclohexene	-	[104]
Mg,Al	2	[W ₇ O ₂₄] ⁶⁻	Anion exchange	-	-	-	[105]
Mg,Al	2	[W ₇ O ₂₄] ⁶⁻	Anion exchange	Epoxidation	Cyclohexene	30.6	[106]
Mg,Al	2	[W ₇ O ₂₄₁ ⁶⁻	Anion exchange	Peroxidation	Cyclohexene	17	[68]
Mg,Al	2	$[H_2W_{12}O_{40}]^{6-}$	Anion exchange	Epoxidation	Cyclooctene	7	[102]
Mg,Al	2	$[W_4Nb_2O_{19}]^{4-}$	Anion exchange	Epoxidation	Cyclooctene	7	[102]
Mg,Al	2	[W ₇ O ₂₄] ⁶⁻	Anion exchange	Sulfoxidation	Dimethylsulfoxide	80	[107]
Mg,Al	2.05	[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Methyl-phenyl-sulfide	18.6	[108]
Mg,Al	2.05	[W ₇ O ₂₄] ⁶⁻	Anion exchange	Oxidation	Dibenzothiophene	<5	[108]
Mg,Al	2.1	[WO ₄] ²⁻	Anion exchange	Oxidation	Methyl-phenyl-sulfide	17.64	[108]
Mg,Al	2.1	$[WO_4]^{2-}$	Anion exchange	Oxidation	Dibenzothiophene	<5	[108]
Mg,Al	2.1	$[WO_4]^{2-}$	Anion exchange	Oxidation	Sec-butyl-sulfide	9.52	[108]
Mg,Al	2.1	[WO ₄] ^{2–}	Anion exchange	Oxidation	Benzothiophene	<5	[108]
Mg,Al	2.57	[WCo ₃ (CoW ₉ O ₃₄) ₂] ¹²⁻	Chimie douce	Epoxidation	Prenol	93.1	[109]
Mg,Al	3	[WO ₄] ²⁻	Anion exchange	Mild oxidative bromination	Aromatics	-	[98]
Ni,Al	3	[WO ₄] ²⁻	Anion exchange	Mild oxidative bromination	Aromatics	-	[98]
Mg,Al	3	[WO ₄] ²⁻	Anion exchange	Sulfoxidation	Dimethylsulfoxide	90	[107]
Mg,Al	3	[PW ₁₁ O ₃₉] ⁷⁻	Anion exchange	Photodegradation	Methyl orange	-	[110]
Mg,Al	3	α -[SiW ₉ O ₃₇ {Co(H ₂ O)} ₃] ¹⁰⁻	Reconstruction	Oxidation	Cyclohexanol	67	[111]
Mg,Al	3	$[WZnMn_2(ZnW_9O_{34})_2]^{12-}$	Anion exchange	Epoxidation	Prenol	87.3	[109]
Mg,Al	3	[PW ₁₁ O ₃₉] ⁷⁻	Anion exchange	Epoxidation	Prenol	84.6	[109]

 Table 9. Summary of LDH with intercalated tungsten-based anions.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Ni,Co	2.57	$[W_2O_7]^{2-}$	Chimie douce	-	-	-	[112]
Ni,Al	2	$[WO_4]^{2-}$	Anion exchange	Mild oxidative bromination	Olefins	21-96	[113]
Ni,Al	2	[WO ₄] ²⁻	Anion exchange	Mild oxidative bromination	Cyclic enol ethers		[106]
Ni,Al	2	$[SiW_{12}O_{40}]^{4-}$	Anion exchange	Epoxidation	Cyclohexene	<30	[114]
Zn,Al	1	[H ₂ W ₁₂ O ₄₀] ⁶⁻	Anion exchange	Öxidation	Isopropanol	10.3	[115]
Zn,Al	1	[SiV ₃ W ₉ O ₄₀] ⁷⁻	Anion exchange	Oxidation	Isopropanol	8	[115]
Zn,Al	2	$[W_{12}O_{41}]^{10-}$	Anion exchange	Photodegradation	Glycerol	-	[116]
Zn,Al	2	[H ₂ W ₁₂ O ₄₀] ⁶⁻	Anion exchange	Epoxidation	Cyclooctene	17	[101]
Zn,Al	2	[H ₂ W ₁₂ O ₄₀] ⁶⁻	Co-precipitation	Peroxidation	Cyclohexene	22	[68]
Zn,Al	2	[W ₄ Nb ₂ O ₁₉] ⁴⁻	Anion exchange	Epoxidation	Cyclooctene	5	[102]
Zn,Al	2	PMo ₁₂ O ₄₀ ³⁻	Anion exchange	Esterification	Acetic Acid	77.23	[86]
Zn,Al	2	[SiW ₁₁ O ₃₉] ⁸⁻	Anion exchange	Photodegradation	Hexachlorocyclohexene	-	[117]
Zn,Al	2	SiW ₁₁ O ₃₉ Mn(H ₂ O) ⁶⁻	Anion exchange	Photodegradation	Hexachlorocyclohexene	-	[117]
Zn,Al	2	$[WCo_3(CoW_9O_{34})_2]^{12-}$	Anion exchange	Epoxidation	Prenol	68.8	[109]
Zn,Al	2	$[WZnMn_2(ZnW_9O_{34})_2]^{12-}$	Anion exchange	Epoxidation	Prenol	88.3	[109]
Zn,Al	3	[SiW ₁₁ O ₃₉] ⁸⁻	Anion exchange	Epoxidation	Cyclohexene	<10	[114]
Zn,Al	3	[SiW ₁₂ O ₄₀] ⁴⁻	Anion exchange	Epoxidation	Cyclohexene	<10	[114]

Table 9. Cont.

Additionally, the results of the epoxidation reaction indicated that $[H_2W_{12}O_{40}]^{6-}$ -intercalated ZnAl-LDH gave the best results in terms of epoxide yield (17% at 24 h). Epoxidation was used also by Liu et al. to verify the catalytic activity of a series of self-assembled polyoxometalate (POM) catalysts that were directly immobilized into layered double hydroxides by a selective ion-exchange method [109]. The sandwich-type POM species are more favorable for the direct immobilization in the LDH structure when compared to Keggin-type POM, because there is no need for rigorous control of the pH [109]. Regarding the catalytic perfromance, the self-assembled polyoxometalate directly immobilized into LDH have achieved up to 99% selectivity of epoxide, 95% H₂O₂ efficiency, and 37,200 h⁻¹ TOF [109].

Wei et al. [103] have obtained a new polyoxometalate anion-pillared LDH by the ionic exchange of an MgAl-LDH precursor in nitrate form with the Keggin-type tungstocobaltate anions $[CoW_{12}O_{40}]^{5-}$, as shown in Figure 13. Powder XRD, together with IR, TG, and cyclic voltammetry, strongly indicated that the guest anions were intercalated in the interlayer space of the resultant material [103]. The catalytic properties of the solid were tested in the oxidation of benzaldehyde with hydrogen peroxide, with high selectivities being obtained [103].



Figure 13. Synthesis route of polyoxotungstates-LDH (POW-LDH) Adapted from Ref. [103], Copyright 2008, Elsevier.

Maciuca et al. [35] performed the catalytic oxidation of different thioethers and thiophene derivatives with H_2O_2 in the presence of W-, V-, and Mo-containing LDH. The solids that were prepared by anion exchange showed good catalytic activity and selectivity but the nature of the intercalated anion influenced their performances [35]. Thus, the W-based LDH was more active and more stable than the V-LDH and Mo-LDH catalysts. Moreover, the conversion of the substrates also depended on their nucleophilicity and, consequently, the following order of reactivity resulted: benzothiophene < dibenzothiophene < diphenyl-sulfide < benzyl-phenyl-sulfide < methyl-phenyl-sulfide [35]. The same group [86] reported the intercalation of tungstate and paratungstate anions in the LDH structure by direct ionic exchange and their use as catalysts for DMSO oxidation in dimethyl sulfone with dilute H_2O_2 . The catalysts performances were strongly influenced by the nature of the cations (Mg²⁺ or Zn²⁺) in the brucite-like layer and by the type of W-anion species ([WO₂]⁴⁻ or [W₇O₂₄]⁶⁻) that are present in the interlayer gallery [107]. The MgAl-LDH-based catalysts exhibited better activity than the ZnAl-LDH type catalysts and the [WO₂]⁴⁻ -containing LDH was more active than the [W₇O₂₄]⁶⁻.

Hulea et al. have also studied the oxidation of thiophenes and thioethers on tungstate-containing LDHs, while analyzing the effect of the relative content of tungstate $[WO_2]^{4-}$ or heptatungstate $[W_7O_{24}]^{6-}$ species on the catalytic performance [108]. A nitrate MgAl-LDH precursor (Mg/Al = 2) that was prepared at pH 9.5 was used to incorporate tungstate by anion exchange at pH 6.5 or 9.5 to obtain $W_7O_{24}^{6-}$ LDH or WO_2^{4-} LDH, respectively. The UV–Vis spectroscopy confirmed the presence of

both tungstate species in both samples. There were some bands at 215–230 nm (tetrahedral [WO₄] species in WO₄^{2–}) and at 250 nm (octahedral [WO₆] species in W₇O₂₄^{6–}) with relative intensities [WO₄]/[WO₆] of 5/1 and 3/1 for the W-LDH and PW-LDH samples, respectively [108]. Finally, Raman spectroscopy showed bands at 980 cm⁻¹ ($\nu_{W=O}$) and 530, 405, and 250 cm⁻¹(δ_{W-O-W}) [108]. Overall, both of the spectroscopies indicated that at pH 9.5 the predominant species is tungstate and at pH 6.5 heptatungstate. Gardner et al. [68] studied the peroxidation of cyclohexene while using [W₇O₂₄]^{6–}-intercalated MgAl-LDH. The poor selectivity observed was corelated to the lack of intracrystalline microporosity under condensed phase reaction conditions [68].

Polyoxotungstates are a challenging and attractive part of the polyoxometalate possessing a variety of structures and topologies that can be used not only in catalysis, but also in photochemistry [104,110,115–117] and electrochemistry [105,112].

4.4. Layered Double Hydroxides Intercalated with Niobium Based Polyoxoanions

Niobium chemistry still remains into semi-obscurity, despite the growing interest of using niobium-based compounds in different applications, ranging from the production of magnets to optical devices and bone implants [118,119]. Niobium materials have also brought important contributions to heterogeneous catalysis, where they are used as catalyst supports or as the active phase [18]. There are not many studies concerning polyoxoniobiates, but those existing (Table 10) sustain that their synthesis occurs under basic pH conditions when compared to polyoxometalates containing V, Mo, or W [120].

The intercalation of niobium-based anions in the structure of layered double hydroxides is a laborious process and it mostly depends on the pH (Table 11) and niobium concentration. Although most of the niobium-based anions intercalated in the interlamellar space of the hydrotalcites are heteropolyoxometalates that are formed by the condensation of WO_x polyhedra around a central niobium atom [102] or NbO_x polyhedra around W [121], there is also reported, in the literature, the synthesis of a POM with the Lindqvist structure, i.e. $[H_3Nb_6O_{19}]^{5-}$, intercalated in a MgAl-LDH [121]. Evans et al. [121] studied the intercalation of some mixed Nb-W POMs (Nb_xW_{6-x}O₁₉^{(x+2)-} where x = 2, 3, 4) within the interlayer region of MgAl-LDH. To avoid the hydrolysis of the precursor materials (LDH or POM) during the anionic exchange, good pH compatibility must exist between them. It was discovered that the niobotungstates [Nb₃W₃O₁₉]⁵⁻ and [Nb₄W₂O₁₉]⁶⁻ are hydrolytically stable when the pH is between 5.5 and 11.5 for the first anion and lower than 8.5 for the second one, which makes them perfectly compatible with MgAl-LDH, which present strong basic properties. [Nb₂W₄O₁₉]⁴⁻ is more suitable for the acidic ZnAl-LDH, due to its increased stability at a pH, ranging from 4.5 to 7.5 [121].

Carriazo et al. also studied mixed Nb-W POM intercalated in LDH [102]. Their work was focused on the synthesis of layered double hydroxides containing different cations within the layers (Al and Mg or Zn) and $[W_4Nb_2O_{19}]^{4-}$ as anion in the interlayers. The PXRD patterns of the prepared materials are characteristic of hydrotalcite-type solids. The intercalation of the tungstoniobate anions has led to higher gallery heights (7.2 Å) when compared to regular hydrotalcites intercalated with nitrate (4 Å) and, as a consequence, the compounds presented microporosity and an increased specific surface area [102]. Moreover, the FTIR results showed that the tungstoniobate anion did not depolymerize and it is entirely located in the interlamellar space. The obtained materials were tested as catalysts in the epoxidation reaction of cyclooctene while using H_2O_2 as oxidant. It was observed that the compounds possess a rather low epoxidation activity (Table 10), but increased catalase activity (decomposition of H_2O_2 to H_2O and O_2) [102]. Carriazo has studied not only the intercalation of mixed Nb-W POMs between the layers of the LDH, but also the synthesis of a new MgAl-LDH intercalated this time with hexaniobate [$H_3Nb_6O_{19}$]⁵⁻.

Layer Cations	Molar Ratio (M ^{II} :M ^{III})	Intercalated Species	Synthesis Method	Reaction	Substrate	Yield (%)	Reference
Mg,Al	1	$[Nb_2W_4O_{19}]^{4-}$	Anion exchange	-	-	-	[121]
Mg,Al	1	[Nb ₃ W ₃ O ₁₉] ⁵⁻	Anion exchange	-	-	-	[121]
Mg,Al	1	[Nb ₄ W ₃ O ₁₉] ⁶⁻	Anion exchange	-	-	-	[121]
Mg,Al	2	$[W_4Nb_2O_{19}]^{4-}$	Anion exchange	Epoxidation	Cyclooctene	7	[102]
Mg,Al	2.1	[H ₃ Nb ₆ O ₁₉] ⁵⁻	Anion exchange	-	-	-	[120]
Zn,Al	2	[W ₄ Nb ₂ O ₁₉] ⁴⁻	Anion exchange	Epoxidation	Cyclooctene	5	[102]

 Table 10. Summary of LDH with intercalated niobium-based anions.

 Table 11. The polymerization degree of oxoniobiate versus pH. Information taken from Ref. [119].

рН	Species			
>14.5	NbO ₂ (OH) ₄ ^{3–}			
14	Nb ₆ O ₁₉ ⁸⁻			
11.5	$H_xNb_6O_{19}^{(8-x)-}$			
6.5	$Nb_{12}O_{36}^{12-}$, $Nb_2O_5 \cdot nH_2O$			
3.65	$Nb_{12}O_{36}^{12-}$, $Nb_2O_5 \cdot nH_2O_5$			
0.55	$Nb_2O_5 \cdot nH_2O$			

The solid was prepared by anion exchange method from the corresponding nitrate LDH precursor and an aqueous solution of $K_8Nb_6O_{19}$ [120]. The PXRD results have indicated the existence of a microporous hydrotalcite-type material, having a gallery height of 7.2 Å, which has the hexaniobate anions oriented with their C_3 axes perpendicular to the layers. The obtained material has a rather small surface area ($24 \text{ m}^2 \text{g}^{-1}$), which considerably increases by calcination at 500 °C (157 m²g⁻¹). However, calcination above 700 °C leads to a decrease of surface area ($45 \text{ m}^2 \text{g}^{-1}$ for the sample calcined at 800 °C) due to crystallization of magnesium niobiate $Mg_4Nb_2O_9$ [120]. Furthermore, the FT-IR studies on the acid-basic properties that were carried out by pyridine and 2-propanol adsorption, showed that the sample obtained through calcination present Lewis-type acid and Brønsted-type basic sites [120]. The niobium chemistry is still a scarcely researched field, which is expected to produce findings that are able to expand the catalysis domain in the near future.

5. Conclusions

Herein, a wide screening of the scientific literature related to the expanded family of POM-LDH composite materials and their use as catalysts for fine organic synthesis is presented. For this investigation, the following three systems hosting polyoxometalates with different nuclearity were analyzed:

- Systems hosting low-nuclearity polyoxometalates, being mainly represented by LDH intercalated with chromate, dichromate, and other different chromium-based anions, such as Cr^{III}(EDTA), [Cr^{III}(SO₃-salen)]²⁻. The prepared materials seemed to offer promising catalytic results, especially in the oxidation of benzyl alcohol and alkoxylation of n-butanol.
- Systems hosting medium-nuclearity polyoxometalates containing LDH intercalated either with molybdenum or vanadium-based anions. Not only Mo-LDH, but also V-LDH, proved to be efficient catalysts for the oxidation and epoxidation reactions. V-LDH was a better catalyst for the epoxidation of alcohols than Mo-LDH. The hydrotalcite containing molybdenum-based anions was also successfully used as a catalyst in reactions, such as condensation, esterification, and halodecarboxylation.
- Systems hosting high-nuclearity polyoxometalates whose primarily representative is LDH intercalated with tungsten-based anions. The catalytic results suggested that the solid is suitable for the epoxidation of alcohols and oxidation of S-containing compounds, such as benzothiophene, dibenzothiophene, benzyl-phenyl sulfide, etc.

The engineering of the POM-LDH materials has been realized through different methods: anionic exchange, co-precipitation, reconstruction, and adsorption mechanisms. All of the studies cited, based on the intercalation of different polyoxometalates in the interlayer space of the hydrotalcites, revealed that the synthesis method can provide POM-LDH materials that are tailored with impressionable redox and acid-base properties. These characteristics can be further improved through the modification of both components (the cations in the brucite-like layers and the polyoxometalate in the interlayer), which makes them suitable materials in many different catalytic processes. POM-LDH materials have an incredibly bright future ahead, being able to exceed other typical catalysts (when it comes to thermal stability, the size, and distribution of the pores). Therefore, it can be strongly sustained that their applications in the catalytic field are theoretically unlimited.

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