



Article Green Epoxidation of Olefins with Zn_xAl/Mg_xAl-LDH Compounds: Influence of the Chemical Composition

Rodica Zăvoianu ^{1,2}, Anca Cruceanu ^{1,2}, Octavian Dumitru Pavel ^{1,2,*}, Corina Bradu ^{3,4}, Mihaela Florea ⁵ and Ruxandra Bîrjega ⁶

- ¹ Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blv., 030018 Bucharest, Romania; rodica.zavoianu@chimie.unibuc.ro (R.Z.); anca.cruceanu@chimie.unibuc.ro (A.C.)
- ² Research Center for Catalysts & Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blv., 030018 Bucharest, Romania
- ³ Faculty of Biology, University of Bucharest, 91-95 Splaiul Independenţei, 050095 Bucharest, Romania; corina.bradu@g.unibuc.ro
- ⁴ Research Center for Environmental Protection and Waste Management (PROTMED), Research Platform in Biology and Systems Ecology, Faculty of Biology, University of Bucharest, 91-95 Splaiul Independenţei, 050095 Bucharest, Romania
- ⁵ National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania; mihaela.florea@infim.ro
- ⁶ National Institute for Lasers, Plasma and Radiation Physics, 077125 Magurele, Romania; ruxandra.birjega@inflpr.ro
- * Correspondence: octavian.pavel@chimie.unibuc.ro; Tel.: +40-21-305-14-64

Abstract: This contribution concerns the effect of the chemical composition of the brucite-type layer of bi-cationic LDH materials Zn_xAl and Mg_xAl (x = 2–5) and tri-cationic LDH Mg_yZn_zAl (y + z = 4, y = 1, 2, 3) on their catalytic activity for olefin epoxidation with H_2O_2 in the presence of acetonitrile. LDH materials were prepared by the standard method of co-precipitation at constant pH 10, using an aqueous solution of the corresponding metal nitrates and a basic solution containing NaOH and Na₂CO₃. The fresh LDHs were calcined to yield the corresponding mixed oxides and then the recovery of the LDH structure by hydration of the mixed oxides was performed. The resulting samples were characterized by AAS, XRD, DRIFT, DR-UV–Vis, BET and determination of basic sites. The results of the catalytic tests for olefin epoxidation were well correlated with the basicity of the samples, which was in turn related to the M^{2+}/Al^{3+} ratio and the electronegativity of different bivalent metals in the brucite-type layer.

Keywords: layered double hydroxides; base catalysts; oxidation; epoxide

1. Introduction

In recent decades, the fine chemical industry started to show a real interest in using base-type heterogeneous catalysts due to the fact that this class of materials presents numerous advantages compared with homogeneous catalysts [1–3], namely: the separation of the catalyst from the reaction products is achieved by a simple filtration, the temperature range in which it can work is often wide, the thermal regeneration of the catalyst is often possible, etc. The layered double hydroxides (LDHs) (discovered in the 19th century [4]), can substitute with good results the corrosive and not environmentally friendly base homogeneous catalysts [4–7]. The LDH general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}] \cdot mH_2O$ where M^{2+} and M^{3+} represent divalent and trivalent cations in the brucite-type layers, A is the interlayer anion with charge n which compensates the excedentary positive charge brought by the isomorphic substitution of M^{2+} with M^{3+} , x is the fraction of the trivalent cation (usually 0.20–0.33) and m is the number of crystallization water molecules [4]. In these structures, the cations adopt octahedral geometry. The mild calcination of LDHs converts them to mixed oxides having an important property named the "*memory effect*",



Citation: Zăvoianu, R.; Cruceanu, A.; Pavel, O.D.; Bradu, C.; Florea, M.; Bîrjega, R. Green Epoxidation of Olefins with Zn_xAl/Mg_xAl-LDH Compounds: Influence of the Chemical Composition. *Catalysts* **2022**, *12*, 145. https://doi.org/ 10.3390/catal12020145

Academic Editor: Anabela A. Valente

Received: 23 December 2021 Accepted: 21 January 2022 Published: 24 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). which consists in the spontaneous structural reconstruction of the original layered structure after hydration with water or aqueous solutions containing different anions [4,8,9]. Through this method, it is possible to include several anions in the interlayer space or to isomorphically exchange the existent cations with others having an adequate radius range. The mixed oxides obtained by calcinations at temperatures higher than 600 °C lose this property because the cations are placed in tetrahedral positions, which have a lower energy state compared to the octahedral ones [10]. Over time, these materials have found applications as catalysts in various fine chemical syntheses [4,11-15]. One class of important reactions are the oxidation ones, which can be classified into two types: one implying only a dehydrogenation and the second one involving both dehydrogenation and oxygen insertion into the hydrocarbon molecule [16]. The difficulties of controlling oxidation reactions in order to avoid total oxidation are due to the fact that usually any oxidation is accompanied by the release of heat, which can make undesirable side reactions thermodynamically possible. Until now, commonly used oxidation agents were NaOCl, alkylperoxides or peroxyacids [17]. However, due to environmental regulations, the actual trend is to replace these oxidants by others which are environmentally friendly, such as H_2O_2 or molecular oxygen, which are considered to be green oxidants [18]. Some oxidation reactions of alkenes give cyclic ethers in which both carbons of a double bond become bonded to the same oxygen atom, products called epoxides or oxiranes with a highly strained cycle which makes those epoxides more reactive than other ethers. Selective epoxidation of olefinic compounds is one of the important steps in organic synthesis of fine chemicals since, by ring opening reactions, epoxides are directly transformed into a wide variety of compounds with excellent yields [19–21]. Among epoxides, epoxycyclohexane is a valuable organic intermediate, used in the synthesis of pharmaceuticals, pesticides, epoxy paints, rubber promoters and stabilizers for chlorinated hydrocarbons [22]. Many publications present the oxidation of cyclohexene to cyclohexene oxide using different solids: magnetic core-shell type Fe₃O₄@chitosan-Schiff base Co(II), Cu(II) and Mn(II) complexes [23], vanadia-based catalysts [24], Ti(III)APO-5 materials [25], Fe nanocatalyst [26], nanostructured Au/SiO₂ [27], Fe(Salen) intercalated-zirconium phosphate [28], niobium oxyhydroxide [29], etc. The green epoxidation of olefins with H_2O_2 was first studied by Payne who showed that a peroxycarboximidic acid serves as a terminal oxygen donor when a nitrile is present as a co-reactant in the presence of a homogeneous base catalyst [30]. The new trend, from the environmental point of view, is using H_2O_2 as an oxidizing agent and different types of LDH solid catalysts, such as: hydrotalcite (HT) [1,31], Cu^{II}(Sal-Ala)/MgAl-LDH and Cu^{ll}(Sal-Phen)/MgAl-LDH [32], hydrotalcite-like compounds with low Mo-loading [33], Mg/Al; Mg,Zn/Al; Mg/Al,Ga hydrotalcite-like compounds [34,35], etc., or molecular oxygen and $M^{II}Mg/Al$ hydrotalcites and hydrotalcite-supported M(II) acetylacetonate (M(II) = Co, Cu or Ni) catalysts [36], cobalt-modified hydrotalcites [17], LDH hosted Fe and Mn sulfonato-salen complexes [37], etc.

The studies published until now concerning the Payne epoxidation with H_2O_2 using hydrotalcite catalysts were limited to the investigation of several factors affecting the selectivity to epoxide such as: the influence of the solvent and the activation agent [1], the influence of the Mg/Al ratio, the presence of pure hydrotalcite phase in the samples, the reconstruction rate of the HT-like phase during the reaction and the addition of water in the reaction mixture [33]. The Mg/Al ratio is a factor particularly influencing the basicity of the catalysts which increases with the Mg content. In a previous work, we investigated the effect of tuning the basicity of the HT structure by inclusion of very small amounts of Zn or Ga in the brucite-type layer on the epoxidation of cyclohexene in the presence of benzonitrile as a reductant agent, showing that Zn- and Ga-containing hydrotalcites presented higher activity than the Mg/Al hydrotalcite for the oxidation of cyclohexene to cyclohexene oxide in the initial stages of the process [34]. One of the issues occurring when Mg/Al LDHs are used as catalysts is that these structures are sensitive to the action of acids such as the peroxycarboximidic acid intermediate formed during Payne epoxidation with H₂O₂. An opportunity to overcome this issue would be the utilization of an LDH structure such as Zn/Al, which possesses the active basic sites but is also more resistant to acid action. To our knowledge, neither pure Zn/Al LDH nor ternary compositions of MgZn/Al with more than 5 mol% Zn in the brucite-type layer have been tested until now as catalysts for cyclohexene epoxidation. There are only two references concerning Zn/Al LDH used as a host for catalytic active guest species such as metallophtalocyanines [38], metatungstate and tungstoniobate [39] in the epoxidation of olefins with O_2 .

Based on the above, the aim of this contribution was to bring new insights into the influence of the chemical composition of a brucite-type layer on the catalytic activity for selective cyclohexene epoxidation with H_2O_2 in the presence of acetonitrile by extending the studies from Mg_xAl to Zn_xAl (x = 1–5) and Mg_yZn_zAl (y + z = 4, y = 1, 2, 3)-type hydrotalcites. It was presumed that the utilization of LDH structures containing larger amounts of Zn in the brucite-type layer could bring the benefit of a better stability towards the action of the peroxycarboximidic acid intermediate. The catalytic performances were determined for all fresh, calcined and reconstructed LDH samples and were correlated with the physico-chemical characteristics of the solids in order to foresee a selection criterion of the optimal composition.

2. Results and Discussion

2.1. Characterization of Catalysts

The chemical compositions of the freshly synthesized samples are presented in Table 1. The results show that the amount of water in the interlayer ranges within 6–18% of the total weight, in concordance with the literature [4].

Samples	The Composition Percent (% Mass)						Mg/Al Molar	Zn/Al	CO ₃ ²⁻ /Al	H ₂ O/Al
Samples	Mg	Zn	Al	CO_{3}^{2-}	NO_3^-	H_2O	Ratio	Molar Ratio	Molar Ratio	Molar Ratio
HT Mg ₂ Al	19.44	n.d.	11.19	14.17	n.d.	17.98	1.93	-	0.57	2.41
HT Mg _{2.5} Al	21.07	n.d.	9.55	11.68	n.d.	15.60	2.45	-	0.55	2.45
HT Mg ₃ Al	22.64	n.d.	8.98	10.98	n.d.	14.97	2.80	-	0.55	2.50
HT Mg ₄ Al	24.86	n.d.	7.46	8.79	n.d.	14.98	3.70	-	0.53	3.01
HT Mg5Al	27.64	n.d.	6.40	7.39	n.d.	11.99	4.80	-	0.52	2.81
HT Zn ₂ Al	n.d.	37.83	8.87	10.25	0.82	12.42	-	1.76	0.52	2.10
HT Zn _{2.5} Al	n.d.	40.44	7.98	9.01	0.91	11.66	-	2.10	0.51	2.20
HT Zn ₃ Al	n.d.	43.20	7.08	8.34	2.12	10.29	-	2.52	0.53	2.18
HT Zn ₄ Al	n.d.	46.65	6.13	7.02	3.25	8.34	-	3.14	0.52	2.04
HT Zn ₅ Al	n.d.	50.75	4.81	5.87	4.48	6.44	-	4.36	0.55	2.01
HT MgZn3Al	4.92	40.12	5.56	6.55	n.d.	10.24	0.98	2.98	0.53	2.76
HT Mg ₂ Zn ₂ Al	11.10	30.21	6.01	6.92	n.d.	10.55	2.05	2.07	0.52	2.63
HT Mg ₃ ZnAl	18.10	16.02	6.67	7.61	n.d.	11.03	3.01	0.99	0.51	2.48

Table 1. The chemical composition of the prepared solid samples.

HT Mg_xAl samples retain more water than HT Zn_xAl ones. Looking at the columns where the molar ratios between each component and Al are presented, it is noticed that the preparation by co-precipitation at pH 10 leads to a lower incorporation of Zn than the one expected considering the molar ratios in the starting solutions, which is in agreement with literature data [40,41]. This effect is less pronounced for Mg, where the molar ratios of Mg/Al are closer to the theoretical ones. An explanation for this effect is that at pH 10, Zn species are more soluble than Mg ones [42,43]. The ratio of CO_3^{2-} /Al always exceeds the theoretical value of 0.5, a fact that may be related to the excess carbonate used in the preparation as well as the high affinity of the cations to this anion. The presence of nitrate ions was evidenced in small concentrations only in the HT Zn_xAl samples. This may be a consequence of the formation of a hydroxynitrate impurity during the co-precipitation and aging of Zn-containing samples [44].

The XRD patterns of the synthesized samples are presented in Figures 1–3 and the calculated structural parameters are presented in the Supplementary Information (Tables S1–S3). The XRD patterns of **HT Mg_xAl** samples present the typical lines of layered materials, as shown in Figure 1 [4,8]. Their intensity decreases with the increase in the Mg/Al ratio because part of Mg forms an amorphous hydroxyde phase [45]. Meanwhile, in the diffraction

patterns of HT Zn_xAl, besides the typical diffraction lines of layered materials, some of the characteristic lines for a zinc hydroxy nitrate $Zn(OH)_4(NO_3)_2$ impurity phase marked with * in Figure 1 are noticed. This additional phase increases its concentration along with x value from 2 to 5, but it is missing in the XRD patterns of HT Mg_yZn_zAl samples. The partial substitution of Mg with Zn leads to the decrease in the crystallinity compared to Mg₄Al and Zn₄Al samples.



Figure 1. The XRD patterns of the freshly prepared HT materials.



Figure 2. The XRD patterns of the calcined materials.



Figure 3. The XRD patterns of the reconstructed samples.

The diffraction patterns of the calcined samples, shown in Figure 2, present the characteristic reflections of the mixed oxides Mg(Al)O (for CHT Mg_xAl) and zincite Zn(Al)O (for CHT Zn_xAl) and a mixture of these oxides in the case of CHT Mg_yZn_zAl samples. The intensity of the diffraction lines for MgO-periclase-type (JCPDS-45-0946) in the patterns of CHT Mg_yZn_zAl decreases with the increase in x. Meanwhile, in the diffraction patterns of CHT Mg_yZn_zAl samples, the periclase-type phase intensity from the corresponding mixed oxides decreases with decreasing amounts of Mg cation to almost nothing for the CHT Mg_Zn_3Al sample.

The diffraction patterns in Figure 3 show that a good reconstruction by the memory effect is possible for a Mg/Al ratio lower than 5, the optimum ratio for a good reconstruction being 3 which is in agreement with literature [4]. For **RHT Zn_xAl** samples, the reconstruction of the layered structure by the memory effect is less pronounced than that noticed for **RHT Mg_xAl** samples. The zincite phase is also always present as an independent phase in the XRD patterns of **RHT Zn_xAl** and **RHT Mg_yZn_zAl** samples, and the intensity of its corresponding maxima denoted with * in Figure 3 increases with Zn content. This aspect was also reported by other authors working with ZnAl LDHs [46].

The DR-UV–Vis spectra of the freshly prepared Zn-containing samples, **HT** Zn_x**Al** and **HT Mg_yZn_zAl**, shown in Figure 4A, show the presence of the band corresponding to Zn(Al)O at 208 nm, in agreement with the findings of XRD analyses. The intensity of this band increases with the Zn content. The spectra of the corresponding RHT samples, shown in Figure 4B, show multiple bands due to the preservation of the Zn(Al)O phase even after hydration. In the spectra of **RHT Mg_yZn_zAl**, it is noticed that the increasing Mg content in the brucite-type layer leads to a shifting of λ_{max} to higher wavelengths (274 < 292 < 300 < 304 nm), indicating a decrease in the M-O bond strength. As a partial conclusion, DR-UV–Vis spectra confirm the poor reconstruction of Zn-containing samples.



Figure 4. DR-UV–Vis spectra of the Zn-modified layered materials; (**A**) freshly prepared HT samples and (**B**) reconstructed samples.

For HT Mg_xAl samples, shown in Figure 5A, it was found that DRIFTS spectra present, in the region $3500-3700 \text{ cm}^{-1}$, a broad band due to the stretching vibration of the OH groups present in the lamellar structures. The position of the maximum is shifted to higher wavenumbers as the Mg/Al ratio increases. A shoulder of this broad band at approx. 3167 cm^{-1} is due to the hydrogen bonds formed with carbonate anions in the interlayer space. The characteristic deformation vibration of water at approx. 1600 cm^{-1} is slightly shifted to higher wavenumbers due to the bridged-type interaction of CO_3^{2-} -H₂O between water molecules and carbonate anions from the interlayer. The effects due to the interaction of carbonate counter ions with superficial hydroxyl groups observed in the spectral region beyond 3000 $\rm cm^{-1}$ are confirmed by specific bands characteristic of the asymmetric stretching vibration (v_3) from free carbonate groups in D_{3h} symmetry in the region from 1420 to 1360 cm⁻¹. The increasing intensity of this band characteristic for carbonate groups certifies the increasing concentration of this compensation anion in the system as the Mg/Al ratio decreases. This conclusion is also supported by the fact that the characteristic peak for carbonate v_4 vibration (700 cm⁻¹) is observed only for samples with Mg/Al ratio < 3 and the characteristic maximum derived from the overlapping of carbonate v_2 and v_1 bands shifts its position from 935 to 1007 cm⁻¹ when the Mg/Al ratio decreases (i.e., as the interlayer carbonate amount increases). An additional band at about 1500 $\rm cm^{-1}$ appears in the spectra of the samples that contain an excedentary brucite-like phase [47,48].

The DRIFT spectra profiles of **HT** Zn_xAl , shown in Figure 5B, are similar to those obtained for Mg_xAl compounds. In the region 3700–3000 cm⁻¹, the band corresponding to hydroxyl groups is shifted towards lower wavenumbers with decreasing Zn/Al ratio (3493; 3507; 3497; 3485 and 3489 cm⁻¹ for Zn/Al ratios = 5; 4; 3; 2.5; 2) as in the case of Mg_xAl compounds. Compared to Mg_xAl solids, the position of the maximum of bands is located at smaller wavenumbers, suggesting a lower basicity of Zn-containing solids. The shift of the shoulder from 3167 cm⁻¹ at 3064 cm⁻¹ (which is more pronounced for Zn_3Al) indicates that the hydrogen bridges of OH ions with the counter anions and water molecules in the interlayer are less intense than in HT Mg_xAl series. The band at 1601 cm⁻¹ (δ_{H2O}) is clearly visible only for the sample richest in Al, Zn_2Al , indicating a lower confinement of water in the interlayer of HT Zn_xAl compared to HT Mg_xAl . In the spectra of the HT Zn_xAl samples, the band characteristic of carbonate around 1423 cm⁻¹ overlaps those characteristic of nitrate. A shift of the maximum to lower wavenumbers is clearly noticed for HT Zn_3Al , HT Zn_4Al and HT Zn_5Al samples which, according to the results of the

chemical analyses, contain higher concentrations of nitrate (see Table 1). By comparing the DRIFT of HT Mg_xAl and HT Zn_xAl , shown in Figure 5A,B, it can be concluded that the first class of materials possess OH groups with a more pronounced basic character.



Figure 5. DRIFT spectra of freshly prepared HT samples: (A) Mg_xAl, (B) Zn_xAl and Mg_yZn_zAl.

The DRIFT spectra of the corresponding mixed oxides, shown in Figure 6A,B, show that the relative intensity of the bands in the region 4000–3000 cm⁻¹ and in the mid-infrared region decreases significantly compared to those in the 1000–400 cm⁻¹ region, indicating that OH groups and even small amounts of carbonate are still present in both series of samples. This fact confirms the literature data claiming that the calcination of the solids at 460 °C does not allow total dehydroxylation and decarbonation [49].

The spectra of **RHT Mg_xAl**, shown in Figure 7A, present the maximum of the band corresponding to v_{OH} shifted by 100 cm⁻¹ to higher wavelengths due to the larger number of OH⁻ introduced by the memory effect compared to the spectra of the **RHT Zn_xAl** samples, shown in Figure 7B, a fact that suggests an increased basicity of the Mg-containing samples. After reconstruction, in the spectra of Zn-containing samples, the band for v_{OH} is less shifted to higher wavenumbers compared to its position in the spectra of corresponding HT samples.

The results in Table 2 point out that the samples in the Zn_xAl series have a smaller specific surface, smaller specific pore volume and larger mesopores compared to those in the Mg_xAl series. The same trend is noticed for the total number of base sites and the weak and medium-strength base sites. As for the number of strong base sites, $HT Zn_4Al$ and $HT Zn_5Al$ have more base sites than the related Mg_xAl samples due to the presence of the zincite phase that has O^{2-} strong base sites.



Figure 6. DRIFT spectra of mixed oxide CHT samples, (A) Mg_xAl, (B) Zn_xAl and Mg_yZn_zAl.



Figure 7. DRIFT spectra of reconstructed RHT samples, (A) Mg_xAl, (B) Zn_xAl and Mg_yZn_zAl.

Sample	S_{sp} (m ² ·g ⁻¹)	Pore Volume (cm ³ ·g ⁻¹)	Pore Radius (Å)	Total Basicity (mmol AA∙g ⁻¹)	Strong Basic Sites (mmol PhOH·g ^{−1})	Weak + Medium Basic Sites * (mmol·g ⁻¹)
HT Mg ₂ Al	141	0.734	207	4.05	0.25	3.80
HT Mg _{2.5} Al	144	0.741	204	4.92	0.32	4.60
HT Mg ₃ Al	89	0.619	251	6.56	0.26	6.30
HT Mg ₄ Al	84	0.592	260	6.95	0.35	6.60
HT Mg ₅ Al	52	0.418	188	7.00	0.10	6.90
HT Zn ₂ Al	103	0.650	239	3.65	0.15	3.50
HT Zn _{2.5} Al	110	0.665	233	3.94	0.24	3.70
HT Zn ₃ Al	83	0.606	256	4.70	0.30	4.40
HT Zn ₄ Al	75	0.549	273	5.47	0.37	5.10
HT Zn ₅ Al	43	0.517	290	6.42	0.42	6.00
HT Mg ₃ ZnAl	136	0.723	211	7.25	0.50	6.75
HT Mg ₂ Zn ₂ Al	102	0.648	240	6.54	0.44	6.10
HT MgZn ₃ Al	76	0.588	263	5.60	0.40	5.20

Table 2. Textural properties and basicities of HT samples.

* The number of weak + medium-strength base sites is given by subtracting the number of strong base sites from the total basicity.

The samples with ternary composition, **HT Mg₃ZnAl** and **HT Mg₂Zn₂Al**, have a larger specific surface area and greater porosity than the reference binary compositions. The total basicity of ternary samples is higher than that of HT Zn₄Al due to the presence of Mg that has a lower Pauling electronegativity than Zn (e.g., 1.31 < 1.65).

The data in Table 3 show a trend of the textural properties and the basicity variation for the calcined samples in the Zn_xAl series compared to those in the Mg_xAl series, similar to that suggested by the data in Table 2 concerning HT samples.

Table 3. Textural properties and basicities of CHT samples.

Sample	$\begin{array}{c} S_{sp} \\ (m^2 \cdot g^{-1}) \end{array}$	Pore Volume (cm ³ ·g ^{−1})	Pore Radius (Å)	Total Basicity (mmol AA∙g ⁻¹)	Strong Basic Sites (mmol PhOH·g ⁻¹)	Weak + Medium Basic Sites * (mmol·g ⁻¹)
CHT Mg ₂ Al	192	0.518	108	6.12	0.16	5.96
CHT Mg _{2.5} Al	196	0.646	110	8.10	0.24	7.86
CHT Mg ₃ Al	188	0.475	150	8.36	0.38	7.98
CHT Mg ₄ Al	230	0.754	120	9.17	0.47	8.70
CHT Mg ₅ Al	198	0.653	109	11.43	0.78	10.65
CHT Zn ₂ Al	140	0.732	206	4.88	0.22	4.66
CHT Zn _{2.5} Al	150	0.784	192	6.41	0.39	6.02
CHT Zn ₃ Al	132	0.433	209	7.40	0.40	7.00
CHT Zn ₄ Al	202	0.662	137	8.59	0.42	8.17
CHT Zn ₅ Al	164	0.537	169	10.50	0.70	9.80
CHT Mg ₃ ZnAl	262	0.859	105	10.50	0.51	9.99
CHT Mg ₂ Zn ₂ Al	248	0.813	118	9.04	0.44	8.60
CHT MgZn ₃ Al	238	0.78	116	8.64	0.43	8.21

* The number of weak + medium-strength base sites is given by subtracting the number of strong base sites from the total basicity.

The textural data displayed in Table 4 show that in the case of the reconstructed samples, the specific surface areas are significantly smaller than those of the HT samples, as was also noticed by other authors who investigated the memory effect [50,51]. However, the trends of the textural properties and the basicity variation for the Zn_xAl series compared to those in the Mg_xAl series are different than those noticed for HT samples (Table 2) and CHT samples (Table 3).

Sample	$\begin{array}{c} S_{sp} \\ (m^2 {\cdot} g^{-1}) \end{array}$	Pore Volume (cm ³ ·g ⁻¹)	Pore Radius (Å)	Total Basicity (mmol AA∙g ⁻¹)	Strong Basic Sites (mmol PhOH·g ^{−1})	Weak + Medium Basic Sites * (mmol∙g ⁻¹)
RHT Mg ₂ Al	15	0.117	285	4.87	0.17	4.70
RHT Mg _{2.5} Al	26	0.183	236	5.96	0.26	5.70
RHT Mg ₃ Al	7	0.025	640	7.21	0.34	6.87
RHT Mg ₄ Al	5	0.018	895	7.42	0.52	6.90
RHT Mg ₅ Al	18	0.141	238	8.47	0.57	7.90
RHT Zn ₂ Al	21	0.164	204	4.68	0.18	4.50
RHT Zn _{2.5} Al	39	0.239	196	5.64	0.24	5.40
RHT Zn3Al	42	0.257	182	5.80	0.30	5.50
RHT Zn ₄ Al	18	0.149	209	6.22	0.42	5.80
RHT Zn5Al	19	0.154	208	7.11	0.51	6.60
RHT Mg ₃ ZnAl	28	0.197	219	8.78	0.58	8.20
RHT Mg ₂ Zn ₂ Al	42	0.296	146	8.25	0.55	7.70
RHT MgZn ₃ Al	34	0.239	180	8.04	0.54	7.50

Table 4. Textural properties and basicities of RHT samples.

* The number of weak + medium-strength base sites is given by subtracting the number of strong base sites from the total basicity.

The fact that Zn-containing samples have larger specific surface areas than the corresponding ones containing Mg may be the consequence of the presence of the zincite secondary phase (indicated in Figure 3) which remains between the reconstructed HT-phase crystallites.

2.2. Catalytic Activity

According to Scheme 1, besides the epoxide compound which is the main product, other by-products appear after some successive and parallel reactions.



Scheme 1. Possible products for the oxidation of cyclohexene (epoxycyclohexane (a); 2-cyclohexene-1-one (b); 2-cyclohexene-1-ol (c); cyclohexane-1,2-diol (d); adipic acid (e)).

The blank test performed without catalyst at 60 °C for 5 h leads to a conversion of cyclohexene of 9.2%, and yield to cyclohexene oxide of 2.5%. The decomposition of hydrogen peroxide in the presence of the catalysts under similar conditions in the absence of cyclohexene and acetonitrile was found to be in the 4–5% range and therefore it was considered that the influence of the solid base catalysts on the decomposition of hydrogen peroxide is low and does not significantly influence the catalytic oxidation of cyclohexene.

The results of the catalytic tests are presented in Figure 8A–C. Since all catalysts were extremely selective for epoxidation, and the total concentration of by-products in the reaction mixture was in the range of 0.5–1 mol%, we have presented the yields to cyclohexeneoxide after 5 h.

The increasing of the Mg/Al ratio from 2 to 5, shown in Figure 8A, led to the increase in the yield to epoxide from 38%, for HT Mg₂Al, up to 82% for HT Mg₅Al. The same trend, but with values lower by around 10%, is noticed for the increasing of the Zn/Al ratio in the same range (e.g., 26% for HT Zn₂Al and 69% for HT Zn₅Al). The lower yield values obtained are a consequence of both the smaller surface areas and the inferior basicity of HT Zn_xAl samples compared to HT Mg_xAl considering the slightly higher electronegativity of Zn (1.65) compared to Mg (1.31). It could also be due to the presence in these samples of the zinc hydroxynitrate impurity. The yield to cyclohexene oxide from the samples with tricationic compositions of Mg_yZn_zAl varies similarly to Mg content, and it is higher than the one obtained from HT Zn₄Al. Only the tricationic HT Mg₃ZnAl sample leads to higher yields than both **HT Zn₄Al** and **HT Mg₄Al**. This fact may be a consequence of its larger specific surface area compared to the reference bi-cationic samples. The mixed oxides show the highest activity of cyclohexeneoxide formation compared to the homologue materials HT and RHT, mostly due to their larger specific surface area and more emphasized basic character, as shown in Figure 8B. The variation of the yield as a function of the chemical composition follows the same trend as the one noticed for the freshly prepared HT materials.



Figure 8. The variation of yield to epoxycyclohexane after 5 h on the investigated catalysts, (**A**) freshly prepared HT samples; (**B**) calcined CHT samples; (**C**) reconstructed RHT samples.

This trend is not noticed for Zn-containing reconstructed samples, shown in Figure 8C. In this case, the sample with the highest activity is **RHT Mg₃ZnAl** instead of **RHT Mg₅Al**. All the RHT samples have higher activity than the corresponding freshly prepared HT samples. As shown in Table 4, the overall basicity of these samples is higher than that of HT (Table 2), even though the specific surface area is smaller. The type of base site is also very important. Di Cosimo et al. [52] showed that the strongest base sites are O^{2-} anions, followed by OH^- , bridge cation-O and hydrogen carbonate or carbonate anions, which are considered as being medium-strength and weak base sites. In several of our early works,

we found that the epoxidation is favored mostly according to the number of weak and medium-strength base sites [33,34]. A correlation of the yield to cyclohexeneoxide and the number of weak and medium-strength base sites of the investigated catalysts is presented in Figure 9.



Figure 9. Variation of the yield to epoxide vs. the number of low- and medium-strength base sites (the colors of the symbols represent the sample compositions: Mg_2Al , Mg_25Al , Mg_3Al , Mg_4Al , Mg_5Al , Zn_2Al , Zn_2Al , Zn_25Al , Zn_3Al , Zn_4Al , Zn_5Al , Mg_3ZnAl , Mg_2Zn_2Al , $MgZn_3Al$).

The possibility of recycling was investigated only for the catalysts that gave yields to cyclohexeneoxide higher than 95% (e.g., CHT Mg4Al, CHT Zn5Al, CHTMg3ZnAl, CHT Mg₅Al). The results obtained in five consecutive cycles are presented in Table 5. For the CHT Mg₅Al sample, the yield decreases after the first cycle with 10%, and falls as low as 75% after the fifth cycle. For CHT Mg_4Al , the yield decreases from 95% to 82% after the first cycle and finally to 64% after the fifth reaction cycle. This behavior is due, on one hand, to the structural modification by reconstruction under the influence of the water and, on the other hand, to the partial dissolution of Mg species by the peroxymidic acid intermediate. The analysis by AAS of the cations from the liquid reaction mixtures obtained after five reaction cycles revealed that the amount of Mg leached from CHT Mg₅Al was around 60 ppm, which corresponded to 2.5% w/w Mg loss from the catalyst, while for CHT Mg₄Al, the leached Mg was 40 ppm, which corresponded to 1.8% w/w Mg loss from the catalyst. The level of Al leached in the reaction mixture was under the detection limit. On the contrary, for CHT Zn₅Al, the yield decreases only by 4.1% after the first reaction cycle (93.6%) and drops to 85.2% after the fifth cycle. This fact is due to the better stability towards the action of the acid intermediate and poor reconstruction ability of the solid. A similar trend is noticed for CHT Mg₃ZnAl which loses only 10% of the yield to cyclohexeneoxide after five reaction cycles, suggesting a synergetic effect between Mg and Zn in this ternary composition. In the case of Zn-containing samples, the levels of cation concentration in the reaction mixtures recovered after five reaction cycles were all under the detection limit. Hence, it seems that the presence of Zn stabilizes the Mg in the framework. This fact was also indicated by the XRD patterns of the materials used in the catalytic tests before and after their regeneration by re-calcination (Figure 10).

Catalyst	Yield to Epoxycyclohexane After 5 h (%)						
Catalyst	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5		
CHT Mg5Al	99.8	89.8	84.3	79.2	75.0		
CHT Mg ₄ Al	95.0	82.0	76.3	69.7	64.0		
CHT Zn ₅ Al	97.7	93.6	89.2	87.5	85.2		
CHT Mg ₃ ZnAl	98.5	95.3	92.4	90.5	88.5		

Table 5. Results obtained in repeated reaction cycles.



Figure 10. XRD patterns of the spent (**A**) (the prefix "s" added to the names of the samples) and recycled samples (**B**) (the prefix "r" added to the names of the samples, diffraction lines corresponding to Mg(Al)O—normal text, diffraction lines of Zn(Al)O—*italics*).

The XRD patterns of the solid samples recovered after the five reaction cycles presented in Figure 10A show that the LDH structure is recovered to some extent during the reaction. Meanwhile, the XRD patterns of the re-calcined samples regenerated after the reaction (Figure 10B) exhibit similar features to those of the parent CHT samples (see Figure 2), showing that the structure is maintained after regeneration.

3. Materials and Methods

3.1. Catalyst Preparation

The catalysts were synthesized using chemicals of analytical purity grade, $Mg(NO_3)_2 \cdot 6H_2O$, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH and Na₂CO₃ were purchased from Merck, Darmstadt, Germany. Three sets of LDH materials were prepared by co-precipitation at pH 10 under low supersaturation conditions [53,54]: (i) Mg_xAl ; (ii) Zn_xAl (with x = 2; 2.5; 3; 4; 5) and (iii) Mg_vZn_zAl (y + z = 4, y = 1, 2, 3). Two aqueous solutions were prepared using the metal nitrate precursors (solution MN) and a mixture of NaOH and Na₂CO₃ (solution B). Solution MN contained the required amounts of dissolved metal nitrates for the desired values of x, y and z, at a total concentration of cations of 1.5 M. Solution B contained a molar amount of Na₂CO₃ 1.5 times higher than the molar amount of Al in the MN solution while the amount of NaOH was adjusted in order to reach a total Na concentration of 3 M. Both solutions were simultaneously fed into the precipitation reactor with a feeding flow of 60 mL·h⁻¹ at room temperature under vigorous stirring at 600 rpm. The obtained gel was aged for 18 h at 75 °C in mother liquor, and cooled afterwards to room temperature. Then, the solid was separated by vacuum filtration and washed with bi-distilled water until the conductivity of the washing water dropped below 100 μ S·cm⁻¹. The washed solids were dried at 90 °C for 24 h under air flow. The freshly prepared solid samples were called

HT Mg_xAl, HT Zn_xAl and HT Mg_yZn_zAl. These materials were calcined at 460 °C for 18 h in air flow to obtain the mixed oxides (CHT Mg_xAl, CHT Zn_xAl, CHT Mg_yZn_zAl). The reconstruction of the hydrotalcite-like structure was performed by immersion of these calcined solids in bi-distilled water for 24 h at 25 °C, followed by drying at 90 °C for 24 h in air flow. The reconstructed materials were named RHT Mg_xAl, RHT Zn_xAl and RHT Mg_yZn_zAl.

3.2. Catalyst Characterization

The chemical composition of the samples was determined by atomic absorption spectrometry (AAS) for the determination of Mg, Zn and Al using a Thermoelemental Solar AAS spectrophotometer (ThermoFischer SCIENTIFIC, Waltham, MA, USA). The inorganic carbon analysis (TIC) was performed with the UV-persulfate oxidation method using a HiPerTOC carbon analyzer (ThermoFischer Scientific, Waltham, MA, USA), which measures the IR absorbance of carbon dioxide produced, and determining weight loss between 105 and 200 °C to determine the amount of hydration water. The total nitrogen content was also determined with the HiPerTOC analyzer using a method based on the catalytic combustion of the samples when the nitrogen is converted into nitric oxide (NO). The NO in the gas outlet from the combustion reactor was further oxidized with ozone in a reaction chamber, generating excited nitrogen dioxide (NO₂*). The emitted radiation by the nitrogen dioxide when returning to the ground state was then quantified by a photomultiplier tube detector.

Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert MPD system (Almelo, Netherlands) equipped with monchromatic CuKα radiation (λ = 1.5418 Å) in a continuous scan mode (counting 2 s/ 0.02° 2θ) over a 5–70° 2θ range. The PANalytical HighScore software package was used for the analysis of the XRD patterns.

DR-UV–Vis spectra were recorded with a Shimadzu 3600 UV–Vis NIR spectrometer (Shimadzu, Kyoto, Japan) equipped with an integration sphere using BaSO₄ as white reference.

DRIFTS spectra obtained from accumulation of 400 scans in the domain $400-4000 \text{ cm}^{-1}$ were recorded with a NICOLET 4700 spectrometer (ThermoFisher Scientific, Waltham, MA, USA). A KBr spectrum was used as background.

 N_2 adsorption–desorption isotherms were determined using a Micromeritics ASAP 2010 instrument (Micromeritics, Eindhoven, Netherlands). Prior to nitrogen adsorption, samples were degassed under vacuum for 24 h.

The basic character of the catalysts was determined using a method based on the irreversible adsorption of organic acids of different pK_a values corresponding to the total number of base sites, e.g., acrylic acid, pK_a = 4.2, and strong base sites, e.g., phenol pK_a = 9.9 [55–58]. The number of weak and medium base sites is given by the difference between the amounts of adsorbed acrylic acid and phenol. The acrylic acid and phenol amounts that remained in solution were determined by UV–Vis spectrometry using the Jasco V650 UV–Vis spectrometer (Jasco, Tokyo, Japan). Three sets of determinations were performed for each solid and the error domaine was +/- 1%.

3.3. Catalytic Tests

The catalytic activity of the solids was tested in the oxidation of cyclohexene with hydrogen peroxide using acetonitrile as a reductant, as shown in Scheme 2 [30,31]. The reactions were performed in a stirred flask (50 mL) at 60 °C, for a 5 h reaction time. In a typical experiment, cyclohexene (4 mmol) and acetonitrile (32 mmol) were dissolved in 20 mL of solvent (mixture of equal volumes of water and acetone). The amount of H_2O_2 was calculated in order to reach a molar ratio of cyclohexene/ H_2O_2 of 1/32 and was added dropwise during the reaction. All reagents were purchased from Merck (Darmstadt, Germany). In all reactions, the catalyst concentration was 1% (w/w) in the reaction mixture. The reaction was monitored in time using a GC K072320 Thermo Quest Chromatograph (ThermoFisher Scientific, Waltham, MA, USA) equipped with an FID detector and a capillary column of 30 m in length with DB5 stationary phase. The oxidation products were

identified by comparison with a standard sample (retention time in GC). The reaction products were also identified by mass spectrometer coupled chromatography, using a GC/MS/MS VARIAN SATURN 2100 T equipped with a CP-SIL 8 CB Low Bleed/MS column of 30 m in length and 0.25 mm in diameter (Varian, Palo Alto, CA, USA). H_2O_2 consumption was determined by an iodometric titration at the end of the reaction. The oxidation process can lead to several products, Scheme 1, such as: epoxycyclohexane (a); 2-cyclohexene-1-one (b); 2-cyclohexene-1-ol (c); cyclohexane-1,2-diol (d); adipic acid (e).



Scheme 2. Reaction mechanism on Brönsted base sites of HT solids.

3.4. Catalyst Recycling

The most active calcined catalysts were selected for recycling tests. The solid catalysts were separated from the reaction mixture by centrifugation and were dried for 5 h at 90 °C and re-calcined at 460 °C for 5 h before being used in the consecutive cycle. XRD patterns of the dried and re-calcined samples after the fifth reaction cycle were recorded. After being analyzed by GC at the end of each cycle, the liquid reaction mixtures recovered for each catalyst were mixed in order to determine the content of cations leached in the liquid using AAS. In order to perform the analysis by AAS, the cations from the liquid samples were extracted in distilled water acidified with HNO₃ (pH 5), and the volume of the aqueous extract was brought to 100 mL in volumetric flasks.

4. Conclusions

The freshly prepared HT Zn_xAl samples contain zinc hydroxynitrate Zn₃(OH)₄(NO₃)₂ as an impurity. This impurity is not present in the samples that contain both Mg and Zn. The calcination of dried samples leads to partial removal of OH groups under H₂O and CO₃^{2–} under the CO₂ form. The reconstruction of the initial structure is not total for Zn-containing LDHs since there are still Zn(Al)O species. The reconstruction is also poor for hydrotalcite samples at a Mg/Al ratio higher than 3. All LDH-derived solids investigated were very selective for cyclohexene epoxidation with H₂O₂ under mild reaction conditions. The catalytic activity and the basicity of the samples varies in the order HT (OH⁻/CO₃^{2–}) < RHT (majority OH⁻) < CHT (O^{2–}). The yield to epoxycyclohexane increases almost linearly when the number of weak and medium-strength base sites in the brucite-type layer rises in the range 4.5–8.5 mmol·g⁻¹. The basicity of Zn-containing

samples decreases proportionally with the amount of Zn incorporated, but Zn improves the stability of the solids towards the action of the acid reaction intermediate and hence the maintenance of the catalytic activity. The strength of the base sites is influenced by the electronegativity of the elements in the brucite-type layer (Mg-containing LDHs have stronger base sites than Zn-containing LDHs) (e.g., Mg 1.31 < Zn 1.65). Based on the obtained results, it could be concluded that the optimal composition of the catalyst enabling a high activity and stability would be that with the ratio Mg/Zn = 3/1 and (Mg + Zn)/Al = 4/1.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal12020145/s1, Table S1. Structural parameters of freshly prepared samples; Table S2. Structural parameters of calcined samples; Table S3. Structural parameters of reconstructed samples.

Author Contributions: Conceptualization, R.Z. and O.D.P.; methodology, R.Z.; investigation, C.B., R.B., O.D.P., R.Z., M.F. and A.C.; resources, R.Z. and M.F.; data curation, R.B.; writing—original draft preparation, R.Z. and O.D.P.; writing—review and editing, R.Z. and O.D.P.; visualization, A.C. and M.F.; supervision, R.B. All authors have read and agreed to the published version of the manuscript.

Funding: APC was sponsored by MDPI.

Data Availability Statement: Not applicable.

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

References

- Romero, M.D.; Calles, J.A.; Ocaña, M.A.; Gómez, J.M. Epoxidation of cyclohexene over basic mixed oxides derived from hydrotalcite materials: Activating agent, solvent and catalyst reutilization. *Microporous Mesoporous Mater.* 2008, 111, 243–253. [CrossRef]
- 2. Schmidt, F. New catalyst preparation technologies- observed from an industrial viewpoint. Appl. Catal. A Gen. 2001, 221, 15–21. [CrossRef]
- 3. Blaser, H.-U.; Studer, M. The role of catalysis for the clean production of fine chemicals. Appl. Catal. A Gen. 1999, 189, 191–204. [CrossRef]
- 4. Cavani, F.; Trifiro, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today* **1991**, *11*, 173–301. [CrossRef]
- Costantino, U.; Curini, M.; Montanari, F.; Nocchetti, M.; Rosati, O. Hydrotalcite-like compounds as catalysts in liquid phase organic synthesis: I. Knoevenagel condensation promoted by [Ni_{0.73}Al_{0.27}(OH)₂](CO₃)_{0.135}. J. Mol. Catal. A Chem. 2003, 195, 245–252. [CrossRef]
- 6. Mantilla, A.; Tzompantzi, F.; Manríquez, M.; Mendoza, G.; Fernández, J.L.; Gómez, R. ZnAlFe mixed oxides obtained from LDH type materials as basic catalyst for the gas phase acetone condensation. *Adv. Mat. Res.* **2010**, *132*, 55–60. [CrossRef]
- 7. Liu, Y.; Lotero, E.; Goodwin, J.G., Jr.; Mo, X. Transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. *Appl. Catal. A Gen.* 2007, 331, 138–148. [CrossRef]
- 8. Pavel, O.D.; Bîrjega, R.; Che, M.; Costentin, G.; Angelescu, E.; Şerban, S. The activity of Mg/Al reconstructed hydrotalcites by "memory effect" in the cyanoethylation reaction. *Catal. Commun.* **2008**, *9*, 1974–1978. [CrossRef]
- Pavel, O.D.; Cojocaru, B.; Angelescu, E.; Pârvulescu, V.I. The activity of yttrium-modified Mg, Al hydrotalcites in the epoxidation of styrene with hydrogen peroxide. *Appl. Catal. A Gen.* 2011, 403, 83–90. [CrossRef]
- 10. Lavikainen, L.P.; Hirvi, J.T.; Kasa, S.; Pakkanen, T.A. Interaction of octahedral Mg(II) and tetrahedral Al(III) substitutions in aluminium-rich dioctahedral smectites. *Theor. Chem. Acc.* 2016, 135, 85. [CrossRef]
- 11. Sels, B.F.; De Vos, D.E.; Jacobs, P.A. Hydrotalcite-like anionic clays in catalytic organic reactions. *Catal. Rev. Sci. Eng.* **2001**, *43*, 443–488. [CrossRef]
- 12. Corma, A.; Iborra, S.; Miquel, S.; Primo, J. Catalysts for the production of fine chemicals: Production of food emulsifiers, monoglycerides, by glycerolysis of fats with solid base catalysts. *J. Catal.* **1998**, 173, 315–321. [CrossRef]
- 13. Ono, Y. Solid base catalysts for the synthesis of fine chemicals. J. Catal. 2003, 216, 406–415. [CrossRef]
- 14. Zhang, F.; Xiang, X.; Li, F.; Duan, X. Layered double hydroxides as catalytic materials: Recent development. *Catal. Surv. Asia* **2008**, 12, 253–265. [CrossRef]
- 15. Tichit, D.; Lutic, D.; Coq, B.; Durand, R.; Teissier, R. The aldol condensation of acetaldehyde and heptanal on hydrotalcite-type catalysts. *J. Catal.* **2003**, *219*, 167–175. [CrossRef]
- 16. Jiao, N.; Stahl, S.S. (Eds.) Green Oxidation in Organic Synthesis; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2019. [CrossRef]
- 17. Angelescu, E.; Ionescu, R.; Pavel, O.D.; Zăvoianu, R.; Bîrjega, R.; Luculescu, C.R.; Florea, M.; Olar, R. Epoxidation of cyclohexene with O₂ and isobutyraldehyde catalysed by cobalt modified hydrotalcites. *J. Mol. Catal. A Chem.* **2010**, *315*, 178–186. [CrossRef]
- Litter, M.I.; Candal, R.J.; Meichtry, J.M. (Eds.) Advanced Oxidation Technologies Sustainable Solutions for Environmental Treatments; CRC Press: Boca Raton, FL, USA, 2014; ISBN 9781138072886.
- 19. Philip, R.M.; Radhika, S.; Abdulla, C.M.A.; Anilkumar, G. Recent trends and prospects in homogeneous manganese-catalysed epoxidation. *Adv. Synth. Catal.* **2021**, *363*, 1272–1289. [CrossRef]

- 20. Dusi, M.; Mallat, T.; Baiker, A. Epoxidation of functionalized olefins over solid catalysts. *Catal. Rev. Sci. Eng.* 2007, 42, 213–278. [CrossRef]
- Hauser, S.A.; Cokoja, M.; Kühn, F.E. Epoxidation of olefins with homogeneous catalysts–Quo vadis? *Catal. Sci. Technol.* 2013, 3, 552–561. [CrossRef]
- Ouidri, S.; Guillard, C.; Caps, V.; Khalaf, H. Epoxidation of olefins on photoirradiated TiO₂-pillared clays. *Appl. Clay Sci.* 2010, 48, 431–437. [CrossRef]
- Cai, X.; Wang, H.; Zhang, Q.; Tong, J.; Lei, Z. Magnetically recyclable core–shell Fe₃O₄@chitosan-Schiff base complexes as efficient catalysts for aerobic oxidation of cyclohexene under mild conditions. J. Mol. Catal. A Chem. 2014, 383–384, 217–224. [CrossRef]
- El-Korso, S.; Khaldi, I.; Bedrane, S.; Choukchou-Braham, A.; Thibault-Starzyk, F.; Bachir, R. Liquid phase cyclohexene oxidation over vanadia based catalysts with tert-butyl hydroperoxide: Epoxidation versus allylic oxidation. *J. Mol. Catal. A Chem.* 2014, 394, 89–96. [CrossRef]
- Alfayate, A.; Márquez-Álvarez, C.; Grande-Casas, M.; Sánchez-Sánchez, M.; Pérez-Pariente, J. Ti(III)APO-5 materials as selective catalysts for the allylic oxidation of cyclohexene: Effect of Ti source and Ti content. *Catal. Today* 2014, 227, 57–64. [CrossRef]
- 26. Habibia, D.; Faraji, A.R.; Arshadi, M.; Fierro, J.L.G. Characterization and catalytic activity of a novel Fe nano-catalyst as efficient heterogeneous catalyst for selective oxidation of ethylbenzene, cyclohexene, and benzylalcohol. *J. Mol. Catal. A Chem.* **2013**, 372, 90–99. [CrossRef]
- 27. Bujak, P.; Bartczak, P.; Polanski, J. Highly efficient room-temperature oxidation of cyclohexene and d-glucose over nanogold Au/SiO₂ in water. *J. Catal.* **2012**, *295*, 15–21. [CrossRef]
- 28. Khare, S.; Chokhare, R. Synthesis, characterization and catalytic activity of Fe(Salen) intercalated α-zirconium phosphate for the oxidation of cyclohexene. *J. Mol. Catal. A Chem.* **2011**, *344*, 83–92. [CrossRef]
- 29. Chagas, P.; Oliveira, H.S.; Mambrini, R.; Le Hyaric, M.; de Almeida, M.V.; Oliveira, L.C.A. A novel hydrofobic niobium oxyhydroxide as catalyst: Selective cyclohexene oxidation to epoxide. *Appl. Catal. A Gen.* **2013**, 454, 88–92. [CrossRef]
- 30. Payne, G.B. Reactions of Hydrogen Peroxide. VII. Alkali-catalyzed epoxidation and oxidation using a nitrile as co-reactant. *J. Org. Chem.* **1961**, *26*, 659–663. [CrossRef]
- 31. Kirm, I.; Medina, F.; Rodriguez, X.; Cesteros, Y.; Salagre, P.; Sueiras, J. Epoxidation of styrene with hydrogen peroxide using hydrotalcites as heterogeneous catalysts. *Appl. Catal. A Gen.* **2004**, *272*, 175–185. [CrossRef]
- Mureşeanu, M.; Georgescu, I.; Bibire, L.E.; Cârjă, G. CU^{II}(Sal-Ala)/MgAlLDH and CU^{II}(Sal-Phen)/MgAlLDH as novel catalytic systems for cyclohexene oxidation by H₂O₂. *Catal. Commun.* 2014, 54, 39–44. [CrossRef]
- 33. Zăvoianu, R.; Bîrjega, R.; Pavel, O.D.; Cruceanu, A.; Alifanti, M. Hydrotalcite like compounds with low Mo-loading active catalysts for selective oxidation of cyclohexene with hydrogen peroxide. *Appl. Catal. A Gen.* **2005**, *286*, 211–220. [CrossRef]
- Angelescu, E.; Pavel, O.D.; Bîrjega, R.; Florea, M.; Zăvoianu, R. The impact of the "memory effect" on the catalytic activity of Mg/Al; Mg,Zn/Al; Mg/Al,Ga hydrotalcite-like compounds used as catalysts for cycloxene epoxidation. *Appl. Catal. A Gen.* 2008, 341, 50–57. [CrossRef]
- 35. Palomeque, J.; Figueras, F.; Gelbard, G. Epoxidation with hydrotalcite-intercalated organotungstic complexes. *Appl. Catal. A Gen.* **2006**, *300*, 100–108. [CrossRef]
- Zăvoianu, R.; Ionescu, R.; Pavel, O.D.; Bîrjega, R.; Angelescu, E. Comparison between Me^{II}Mg/Al hydrotalcites and hydrotalcitesupported Me(II) acetylacetonates (Me(II) = Co, Cu or Ni) catalysts for the epoxidation of cyclohexene with molecular oxygen. *Appl. Clay Sci.* 2011, 52, 1–10. [CrossRef]
- 37. Bhattacharjee, S.; Anderson, J.A. Comparison of the epoxidation of cyclohexene, dicyclopentadiene and 1,5-cyclooctadiene over LDH hosted Fe and Mn sulfonato-salen complexes. *J. Mol. Catal. A Chem.* **2006**, *249*, 103–110. [CrossRef]
- Zhou, W.; Zhou, J.; Chen, Y.; Cui, A.; Sun, F.; He, M.; Xu, Z.; Chen, Q. Metallophthalocyanine intercalated layered double hydroxides as an efficient catalyst for the selective epoxidation of olefin with oxygen. *Appl. Catal. A Gen.* 2017, 542, 191–200. [CrossRef]
- 39. Carriazo, D.; Lima, S.; Martín, C.; Pillinger, M.; Valente, A.A.; Rives, V. Metatungstate and tungstoniobate-containing LDHs: Preparation, characterisation and activity in epoxidation of cyclooctene. *J. Phys. Chem. Solids* **2007**, *68*, 1872–1880. [CrossRef]
- 40. Seftel, E.M.; Popovici, E.; Mertens, M.; De Witte, K.; Van Tendeloo, G.; Cool, P.; Vansant, E.F. Zn–Al layered double hydroxides: Synthesis, characterization and photocatalytic application. *Microporous Mesoporous Mater.* **2008**, *113*, 296–304. [CrossRef]
- 41. Tzompantzi, F.; Mantilla, A.; Banũelos, F.; Fernández, J.L.; Gómez, R. Improved photocatalytic degradation of phenolic compounds with znal mixed oxides obtained from LDH Materials. *Top. Catal.* **2011**, *54*, 257–263. [CrossRef]
- 42. Krężel, A.; Maret, W. The biological inorganic chemistry of zinc ions. Arch. Biochem. Biophys. 2016, 611, 3–19. [CrossRef]
- 43. Scholz, F.; Kahlert, H. The calculation of the solubility of metal hydroxides, oxide-hydroxides, and oxides, and their visualisation in logarithmic diagrams. *ChemTexts* **2015**, *1*, 7. [CrossRef]
- 44. Moezzi, A.; Lee, P.-S.; McDonagh, A.M.; Cortie, M.B. On the thermal decomposition of zinc hydroxide nitrate, Zn₅(OH)₈(NO₃)₂·2H₂O. *J. Solid State Chem.* **2020**, *286*, 121311. [CrossRef]
- 45. Angelescu, E.; Pavel, O.D.; Zavoianu, R.; Birjega, R. Cyanoethylation of ethanol over mixed oxides obtained from hydrotalcite, precursors. *Rev. Roum. Chim.* 2004, *49*, 367–375.
- 46. Starukh, G.; Rozovik, O.; Oranska, O. Organo/Zn-Al LDH nanocomposites for cationic dye removal from aqueous media. *Nanoscale Res. Lett.* **2016**, *11*, 228. [CrossRef]

- Navajas, A.; Arzamendi, G.; Romero-Sarria, F.; Centeno, M.A.; Odriozola, J.A.; Gandía, L.M. DRIFTS study of methanol adsorption on Mg–Al hydrotalcite catalysts for the transesterification of vegetable oils. *Catal. Commun.* 2012, 17, 189–193. [CrossRef]
- 48. Kocík, J.; Hájek, M.; Tišler, Z.; Strejcová, K.; Velvarská, R.; Bábelová, M. The influence of long-term exposure of Mg–Al mixed oxide at ambient conditions on its transition to hydrotalcite. *J. Solid State Chem.* **2021**, *304*, 122556. [CrossRef]
- Yi, H.; Zhao, S.; Tang, X.; Ning, P.; Wang, H.; He, D. Influence of calcination temperature on the hydrolysis of carbonyl sulfide over hydrotalcite-derived Zn–Ni–Al catalyst. *Catal. Commun.* 2011, *12*, 1492–1495. [CrossRef]
- 50. Takehira, K.; Kawabata, T.; Shishido, T.; Murakami, K.; Ohi, T.; Shoro, D.; Honda, M.; Takaki, K. Mechanism of reconstitution of hydrotalcite leading to eggshell-type Ni loading on Mg single bondAl mixed oxide. *J. Catal.* 2005, 231, 92–104. [CrossRef]
- 51. Palomeque, J.; Lopez, J.; Figueras, F. Epoxydation of activated olefins by solid bases. J. Catal. 2002, 211, 150–156. [CrossRef]
- 52. Di Cosimo, J.I.; Díez, V.K.; Xu, M.; Iglesia, E.; Apesteguía, C.R. Structure and surface and catalytic properties of Mg-Al basic oxides. *J. Catal.* **1998**, *178*, 499–510. [CrossRef]
- 53. Corma, A.; Fornes, V.; Rey, F. Hydrotalcites as Base Catalysts: Influence of the Chemical Composition and Synthesis Conditions on the Dehydrogenation of Isopropanol. *J. Catal.* **1994**, *148*, 205–212. [CrossRef]
- Jyothi, T.M.; Raja, T.; Sreekumar, K.; Talawar, M.B.; Rao, B.S. Influence of acid–Base properties of mixed oxides derived from hydrotalcite-like precursors in the transfer hydrogenation of propiophenone. J. Mol. Catal. A Chem. 2000, 157, 193–198. [CrossRef]
- 55. Debecker, D.; Gaigneaux, E.M.; Busca, G. Exploring, tuning, and exploiting the basicity of hydrotalcites for applications in heterogeneous catalysis. *Chem. Eur. J.* **2009**, *15*, 3920–3935. [CrossRef] [PubMed]
- 56. Parida, K.; Das, J. Mg/Al hydrotalcites: Preparation, characterisation and ketonisation of acetic acid. J. Mol. Catal. A Chem. 2000, 151, 185–192. [CrossRef]
- 57. Ionescu, R.; Pavel, O.D.; Bîrjega, R.; Zăvoianu, R.; Angelescu, E. Epoxidation of cyclohexene with H₂O₂ and acetonitrile catalyzed by Mg–Al hydrotalcite and cobalt modified hydrotalcites. *Catal. Lett.* **2010**, *134*, 309–317. [CrossRef]
- Pavel, O.D.; Zăvoianu, R.; Bîrjega, R.; Angelescu, E. The effect of ageing step elimination on the memory effect presented by Mg_{0.75}Al_{0.25} hydrotalcites (HT) and their catalytic activity for cyanoethylation reaction. *Catal. Commun.* 2011, 12, 845–850. [CrossRef]