

Article

## Selective Oxidation of Glycerol with 3% H<sub>2</sub>O<sub>2</sub> Catalyzed by LDH-Hosted Cr(III) Complex

Gongde Wu, Xiaoli Wang \*, Taineng Jiang and Qibo Lin

Department of Environment and Technology, Nanjing Institute of Technology, Nanjing 211167, China; E-Mails: wugongde@njit.edu.cn (G.W.); jtn0825@163.com (T.J.); linqibo0908@163.com (Q.L.)

\* Author to whom correspondence should be addressed; E-Mail: wangxiaoli212@njit.edu.cn; Tel./Fax: +86-25-86118960.

Academic Editor: Stuart H. Taylor

Received: 22 October 2015 / Accepted: 23 November 2015 / Published: 27 November 2015

---

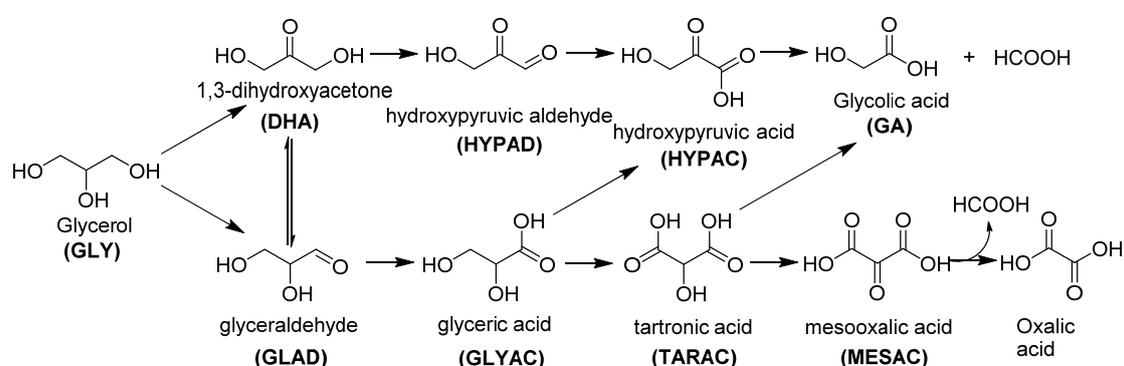
**Abstract:** A series of layered double hydroxides (LDHs) –hosted sulphonato-salen Cr(III) complexes were prepared and characterized by various physico-chemical measurements, such as Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), powder X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM) and elemental analysis. Additionally, their catalytic performances were investigated in the selective oxidation of glycerol (GLY) using 3% H<sub>2</sub>O<sub>2</sub> as an oxidant. It was found that all the LDH-hosted Cr(III) complexes exhibited significantly enhanced catalytic performance compared to the homogeneous Cr(III) complex. Additionally, it was worth mentioning that the metal composition of LDH plates played an important role in the catalytic performances of LDH-hosted Cr(III) complex catalysts. Under the optimal reaction conditions, the highest GLY conversion reached 85.5% with 59.3% of the selectivity to 1,3-dihydroxyacetone (DHA). In addition, the catalytic activity remained after being recycled five times.

**Keywords:** layered-double hydroxides; Cr(III) complex; 1,3-dihydroxyacetone; glycerol

---

## 1. Introduction

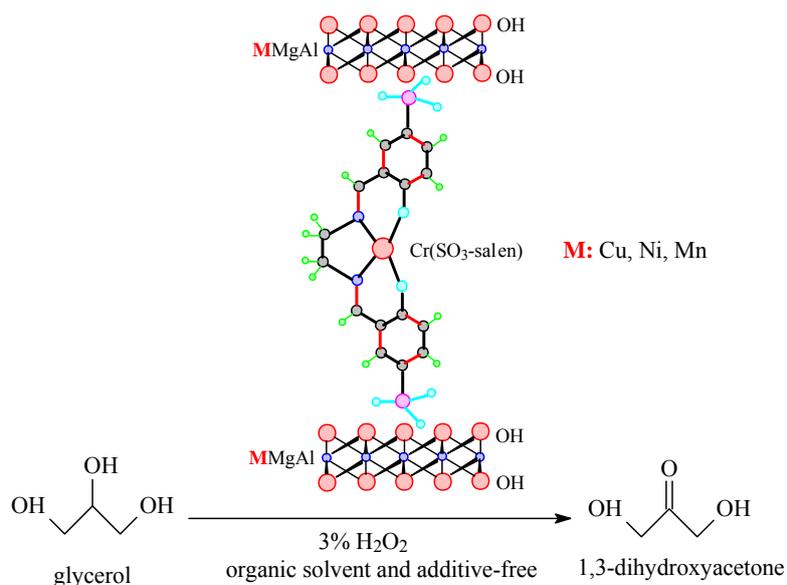
GLY is an unavoidable by-product of the biodiesel process, and with every 9 kg of biodiesel produced, about 1 kg of GLY is left behind. So, to convert GLY into a high-value chemical is of great importance for the biodiesel industry, and it represents a great challenge [1–4]. Among the various valuable conversions of GLY, in the context of atom economy, the oxidation of GLY could be more economical. However, the oxidation of GLY leads to a diverse reaction pathway (see Scheme 1), and the selectivity is difficult to control. The oxidation products of GLY, such as 1,3-dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLYAC), hydroxypyruvic acid (HYPAC), Glycolic acid (GA), tartronic acid (TARAC), mesooxalic acid (MESAC), *etc.*, often distribute wildly [5,6]. Therefore, there is an urgent need to design new, effective, heterogeneous catalysts for controlling the chemoselective orientation of GLY oxidation.



**Scheme 1.** A possible reaction pathway of glycerol oxidation.

To date, there have been many studies on the heterogeneous catalytic oxidation of GLY over noble metal catalysts [7–13]. However, noble metal catalysts often suffered from the drawbacks of high cost and easy deactivation, so the design of effective low-cost transition metal catalysts attracted more and more attention in the past decade [1,6,14–18]. Zhou *et al.* found that Cu-containing layered double hydroxide (LDH) was effective for the selective oxidation of GLY by O<sub>2</sub>, and the main product was GLYAC with a yield of 68% [4]. McMorn *et al.* studied the selective oxidation of GLY over a range of transition metal-containing silicates and aluminophosphate catalysts, but the main products were the low-value formic acid and a mono-formate ester of GLY [6]. Crotti *et al.* prepared iron complexes for the oxidation of GLY by H<sub>2</sub>O<sub>2</sub>, and the main products were DHA and formic acid [16]. Generally, the possibility of glycerol oxidation over transition metal catalysts is rarely reported, so it was significant to design a highly effective transition metal heterogeneous catalyst for the selective oxidation of GLY.

In our previous article, we briefly reported that a MgAl LDH-hosted Cr(III) complex was effective in the selective oxidation of GLY [15]. It is well known that different divalent or trivalent metal elements can be assembled onto the plates of LDHs. Thus, it was essential to make an in-depth study of the element composition of LDH plates, which could significantly influence the catalytic performance of LDH-hosted catalysts. In the present work, a series of binary and ternary LDHs as well as their hosted complexes were prepared, and the roles of LDH plates in the catalytic performance of LDH-hosted catalysts were investigated in the organic solvent-free selective oxidation of GLY into DHA with 3% H<sub>2</sub>O<sub>2</sub> (Scheme 2).



**Scheme 2.** Selective oxidation of GLY to DHA on LDH-hosted Cr(III) complex.

## 2. Results and Discussion

### 2.1. Characterization of Catalysts

The results in Table 1 show that the molar ratios of metals in binary LDHs and ternary LDHs were similar, indicating that the nature of metals but not the molar ratios of metals in LDHs would afford their different catalytic performance. Simultaneously, the molar ratios of metals in LDH-hosted complexes were found to be almost the same as those of their corresponding LDH carriers, which suggested that no element loss occurred during the intercalation of the Cr(III) complex. Furthermore, chemical analysis revealed that the obtained values of the Cr(salen) complex were quite comparable with the calculated values; meanwhile, the C/N and N/Cr molar ratios of all LDH-hosted complexes were consistent with the value in the homogeneous Cr(III) complex. This indicated that the as-prepared LDH-hosted catalysts held the expected elemental composition as the structure of the catalyst depicted in Scheme 2. Moreover,  $\text{C}_6\text{H}_5\text{COO}^-$  anions had been completely exchanged out of LDH interlayers by the sulphonato-salen Cr(III) complex during the ion exchange process. However, a significant decrease in the surface area of LDH-hosted complexes was observed in comparison with that of their carriers, which might be attributed to the introduction of the Cr(III) complex with large space size.

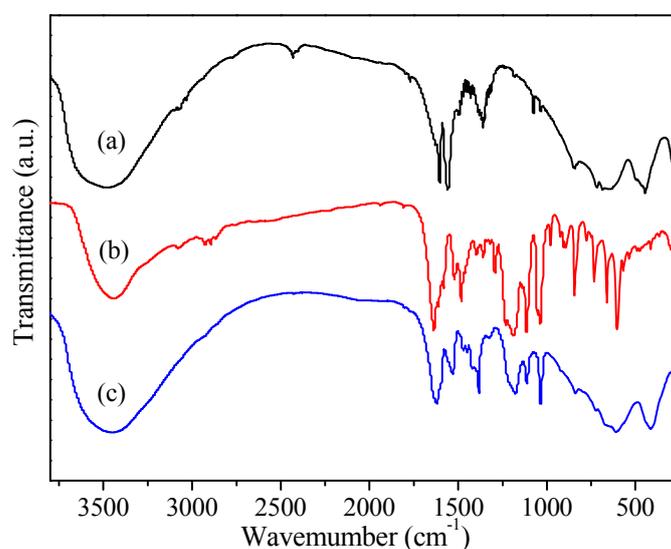
Considering the similarity of LDH-hosted Cr( $\text{SO}_3\text{-salen}$ ) samples with different element compositions of LDH carriers in spectroscopic characterization, Cr( $\text{SO}_3\text{-salen}$ )-CuMgAl-LDH was selected as a typical catalyst for comparison with Cr( $\text{SO}_3\text{-salen}$ ) and CuMgAl-LDH. The FTIR spectrum of the homogeneous Cr( $\text{SO}_3\text{-salen}$ ) complex showed the characteristic bands at 1636, 1602, 1520, 1480, 1290, 1110, 1035  $\text{cm}^{-1}$  (see Figure 1), which fit well with the published data in the literature [19]. The assignments of the representative bands for the successful preparation of the Cr(salen) complex with a tetradentate ONNO functionality were the bands at 1636  $\text{cm}^{-1}$  due to the C=N stretching vibration of the imine groups, along with the bands at 1110 and 1035  $\text{cm}^{-1}$  due to the anti-symmetric and symmetric stretching modes of the  $\text{SO}_3^-$  moiety [20,21]. In the FTIR spectra of LDH-hosted complex materials, apart from the bands in the overlapping regions of the hydroxide backbone, the other bands of the

Cr(salen)-SO<sub>3</sub> complex were all clearly observed, though there were some marginal shifts in the position of bands due to the intercalation. This indicated that the quadridentate coordination structures in the homogeneous complex all survived from the intercalation in spite of the differences in the element composition of LDH carriers. Furthermore, in FTIR spectra of the LDH-hosted complexes, the characteristic bands of C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup> anions (1550 cm<sup>-1</sup>) no longer appeared [18], also suggesting that the ion exchange process was complete, which was consistent with the results of chemical analysis.

**Table 1.** Components and textural parameters of samples.

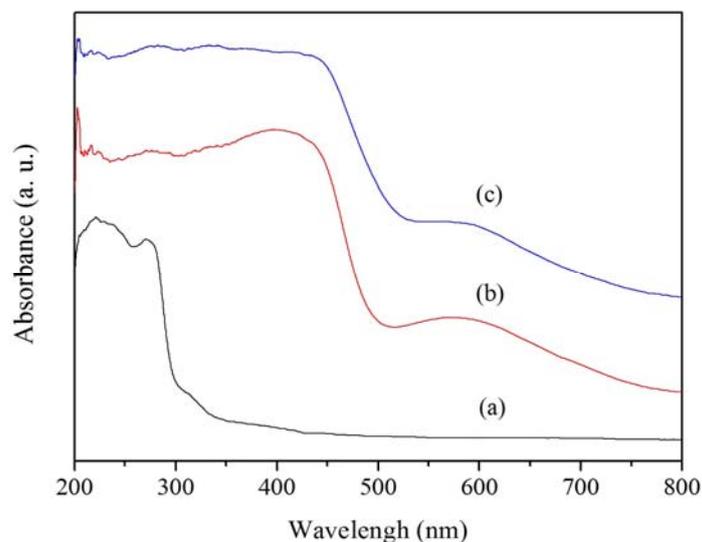
Samples	Elemental Analysis Data (wt. %)							S <sub>BET</sub> (m <sup>2</sup> /g)
	C	H	N	Cr	Molar Ratio	C/N <sup>a</sup>	N/Cr <sup>b</sup>	
MgAl-LDH	-	-	-	-	Mg/Al = 3/1	-	-	80.2
NiAl-LDH	-	-	-	-	Ni/Al = 3/1	-	-	82.5
ZnAl-LDH	-	-	-	-	Zn/Al = 3/1	-	-	81.7
MgCr-LDH	-	-	-	-	Mg/Cr = 3/1	-	-	82.0
MnMgAl-LDH	-	-	-	-	Mn/Mg/Al = 0.86/0.84/1.00	-	-	80.5
CoMgAl-LDH	-	-	-	-	Co/Mg/Al = 0.85/0.84/1.00	-	-	78.9
NiMgAl-LDH	-	-	-	-	Ni/Mg/Al = 0.86/0.85/1.00	-	-	79.5
CuMgAl-LDH	-	-	-	-	Cu/Mg/Al = 0.88/0.88/1.00	-	-	80.2
ZnMgAl-LDH	-	-	-	-	Zn/Mg/Al = 0.87/0.85/1.00	-	-	78.4
Cr(SO <sub>3</sub> -salen)	42.45 (42.46) <sup>c</sup>	2.64 (2.65)	6.17 (6.19)	11.51 (11.50)	-	8.03 (8.00)	1.99 (2.00)	-
Cr(SO <sub>3</sub> -salen)- CuMgAl-LDH	23.51	2.84	3.42	6.35	Cu/Mg/Al = 0.87/0.88/1.00	8.02 (8.00)	2.01 (2.00)	66.3
Cr(SO <sub>3</sub> -salen)- NiMgAl-LDH	23.41	2.83	3.41	6.33	Ni/Mg/Al = 0.87/0.86/1.00	8.01 (8.00)	2.00 (2.00)	65.5
Cr(SO <sub>3</sub> -salen)- MnMgAl-LDH	23.20	2.80	3.38	6.36	Mn/Mg/Al = 0.86/0.85/1.00	8.00 (8.00)	1.99 (2.00)	65.8

<sup>a</sup> The molar ratio of C to N; <sup>b</sup> The molar ratio of N to Cr; <sup>c</sup> The data in parentheses are the theoretical values calculated from the structure of the catalyst in Scheme 2.



**Figure 1.** FTIR spectra of (a) CuMgAl-LDH; (b) Cr(SO<sub>3</sub>-salen); (c) Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH.

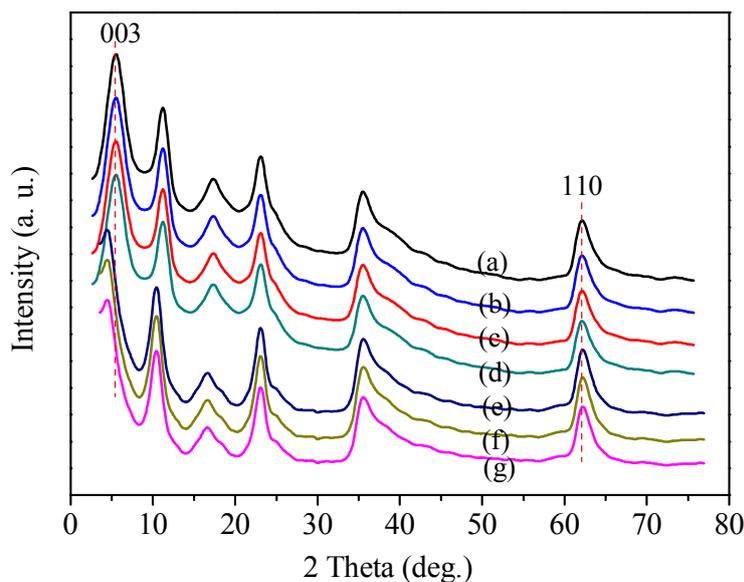
Completely different from the UV-vis spectrum of the LDH carrier, the homogeneous complex displayed a peak at about 410 nm typical of the metal-ligand band and a broad peak at about 580 nm associated with d-d transitions (see Figure 2). This was similar to related metal salen compounds described in the literature [22,23], indicating the successful preparation of the Cr(III) complex. The UV-vis spectrum of the LDH-hosted complex was quite similar to the spectrum of the neat complex, further confirming that the LDH-hosted complexes were all successfully prepared.



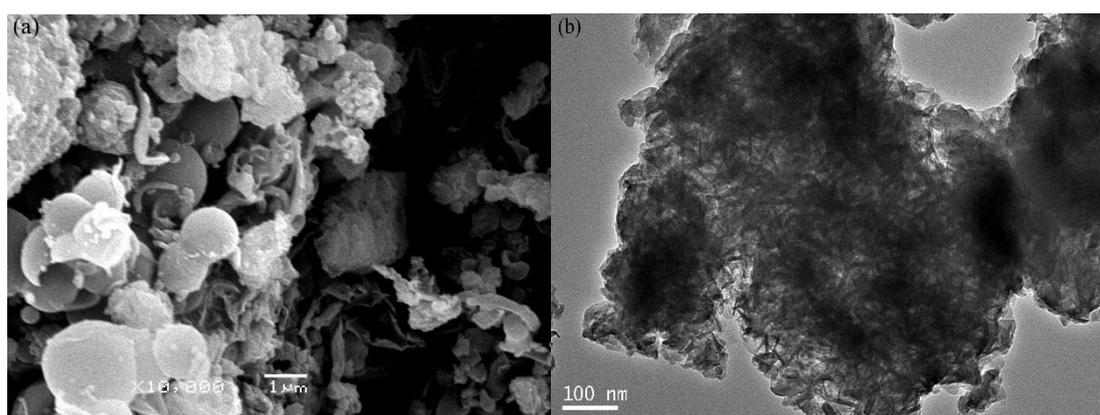
**Figure 2.** UV-vis spectra of (a) CuMgAl-LDH; (b) Cr(SO<sub>3</sub>-salen); (c) Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH.

As detected by the powder XRD (see Figure 3), all LDH carriers and the LDH-hosted complexes were proved typical of layered materials [24–26]. A sharp peak at the (003) plane indicated the formation of a highly crystalline material, and was related to the interlayer distance dependent on the anion size and electrostatic force in the hydroxalcite-like interlayer. The peak at the (110) plane corresponded to the atomic distributed density dependent on the Mg/Al molar ratio. Compared to the binary LDH, the ternary LDHs exhibited almost the same XRD patterns, indicating that the presence of the third metal did not affect the LDH structure. However, LDH-hosted complexes showed an increase in  $d_{003}$  without the change in  $d_{110}$  in comparison with their corresponding LDH carriers. This indicated that the basal spacing in the LDH interlayer increased due to the introduction of the Cr(III) complex, while no loss of the metal element occurred.

Typically, the SEM and TEM images of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH are shown in Figure 4. From the SEM picture, it was found that LDH materials form plate-like agglomerated crystals, while the TEM image of the sample exhibited typical hydroxalcite-like layered structures. In addition, the particle size distribution was about 20–50 nm.



**Figure 3.** XRD patterns of (a) MgAl-LDH; (b) CuMgAl-LDH; (c) NiMgAl-LDH; (d) MnMgAl-LDH; (e) Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH; (f) Cr(SO<sub>3</sub>-salen)-NiMgAl-LDH; (g) Cr(SO<sub>3</sub>-salen)-MnMgAl-LDH.



**Figure 4.** (a) SEM and (b) TEM images of LDH-[Cu(SO<sub>3</sub>-salen)].

## 2.2. Catalytic Performances of Catalysts

The catalytic performances of the as-prepared catalysts were investigated in the selective oxidation of GLY. No organic solvent, additive or phase transfer catalyst was used. Under the conditions used herein, only six products, DHA, GLYAC, GA, TARAC, formic acid and oxalic acid, were detected. Other products, if any, present as minor constituents could not be detected.

The results in Table 2 showed that, when binary LDHs were used as catalysts, with the exception of a spot of DHA and GLYAC, all other product compounds were the result of an over-oxidation reaction. Moreover, among the two partial oxidation products, the C<sub>3</sub> oxygenated products of primary alcohol-GLYAC dominated the C<sub>3</sub> oxygenated products of secondary alcohol-DHA. This indicated that the obtained catalysts were more active for the oxidation of primary alcohol. It was also found that all the binary catalysts, except MgAl-LDH, exhibited the conversion of GLY below 5%. In the

presence of MgAl-LDH, the optimal GLY conversion reached 12.5% with 6.5% of the selectivity to GLYAC.

**Table 2.** Catalytic performance of LDH samples in GLY oxidation <sup>a</sup>.

Catalyst	GLY Con. (mol·%)	Sel. (mol·%)					
		DHA	GLYAC	TARAC	GA	Oxalic Acid	Formic Acid
MgAl-LDH	12.5	0	6.5	0	10.0	1.2	82.3
NiAl-LDH	4.5	0	3.0	2.5	13.5	1.5	79.5
ZnAl-LDH	5.0	0.3	4.5	1.6	17.6	2.2	73.8
MgCr-LDH	4.5	0.2	6.2	0.5	22.5	1.5	69.1
MnMgAl-LDH	14.2	0.2	10.7	1.5	20.6	2.0	65.0
CoMgAl-LDH	12.0	0	7.6	0	20.2	0	72.2
NiMgAl-LDH	25.5	0.5	19.5	3.7	15.0	1.4	59.9
CuMgAl-LDH	36.5	0	30.2	0	12.2	2.1	55.5
ZnMgAl-LDH	12.7	0	5.7	0	13.5	2.0	78.8

<sup>a</sup> Reaction conditions: GLY (50 mL, 0.2 mol·L<sup>-1</sup>), 3% H<sub>2</sub>O<sub>2</sub> (30 mL), 0.2 g catalyst, 60 °C, 6 h.

MgAl-LDH, the most active binary LDH catalyst, was then chosen to introduce the third metal element (Cu, Ni, Mn and Co) by the means of assembling different cations on LDH plates. The obtained trinary LDH catalysts were also used for the selective oxidation of GLY, and the results were also listed in Table 2. It was found that the different metal species had a distinct influence on the catalytic performance of trinary LDH catalysts. Among them, no significant difference in catalytic performance was found over the catalyst of CoMgAl-LDH and ZnMgAl-LDH, while the other trinary LDH catalysts exhibited much higher catalytic performance than MgAl-LDH. Particularly in the presence of CuMgAl-LDH, the GLY conversion was remarkably increased to 36.5% with 30.2% selectivity to GLYAC. These results suggested that Cu was the excellent active metal species for the GLY selective oxidation reaction.

In virtue of the exchangeable property of anions in interlayers of LDH, Cr(SO<sub>3</sub>-salen) was introduced into LDH interlayers by the ion exchange reaction. The catalytic performance of the obtained LDH-hosted complex catalysts were also investigated in the selective oxidation of GLY (see Table 3). With homogeneous Cr(SO<sub>3</sub>-salen) used as a catalyst, 38.2% of GLY conversion was found; simultaneously, compared to the LDH catalysts in Table 2, the selectivity to DHA significantly improved (11.5%). This indicated that the sulphonato-salen Cr(III) complex was effective for the oxidation of C<sub>3</sub> secondary alcohol. Interestingly, upon the homogeneous Cr(III) complex being introduced into the LDHs, the GLY conversion further increased sharply. In the presence of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH, the optimal GLY conversion of 85.5% was obtained, and the main product was the partial oxidation product of DHA (Sel. 59.3%). This could be attributed to the synergistic catalysis between the Cr(III) complex and LDH carriers. On the one hand, the substantial surface free silicon alcohol in LDHs tended to form H-bonding with the hydrogen atom of H<sub>2</sub>O<sub>2</sub>, which could significantly improve the oxidation capacity of H<sub>2</sub>O<sub>2</sub>. On the other hand, the weak base environment could also enhance the catalytic performance by facilitating the formation of intermediate product alkoxide [7].

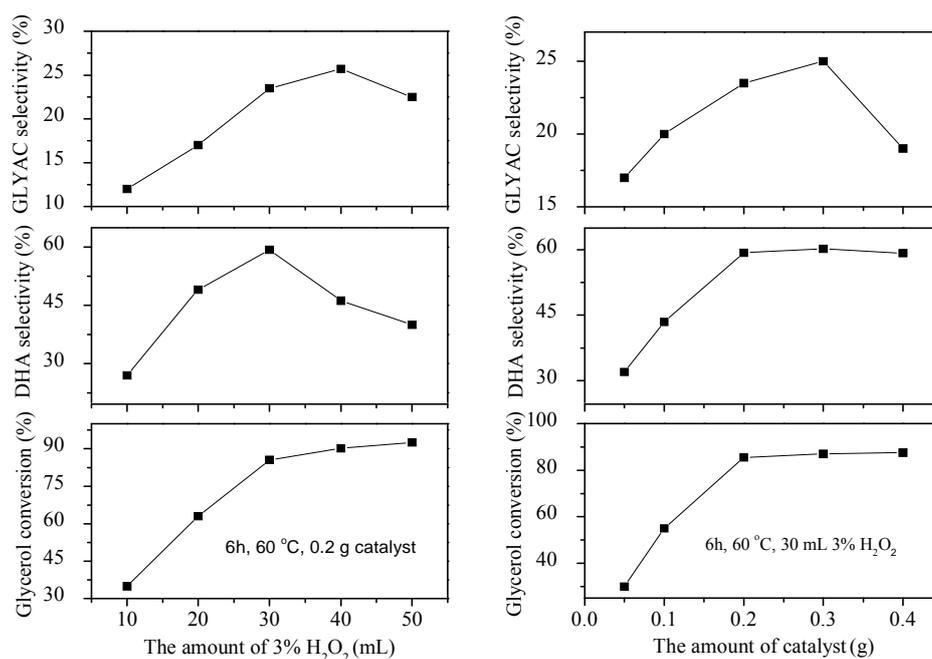
**Table 3.** Catalytic performance of complex samples in GLY oxidation <sup>a</sup>.

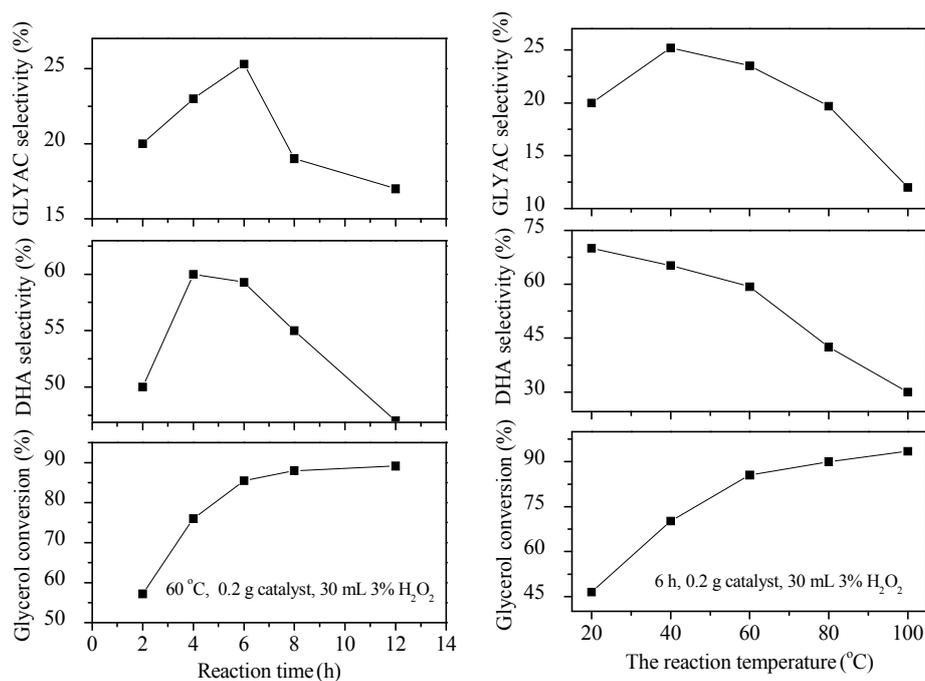
Catalyst	GLY Con. (mol·%)	Sel. (mol·%)					
		DHA	GLYAC	TARAC	GA	Oxalic Acid	Formic Acid
Cr(SO <sub>3</sub> -salen)	38.2	11.5	13.9	0	0	0.3	74.3
Cr(SO <sub>3</sub> -salen)-CuMgAl-LDH	85.5	59.3	23.5	2.5	0	2.4	12.3
Cr(SO <sub>3</sub> -salen)-NiMgAl-LDH	82.1	61.2	28.5	0	0	0.3	10.0
Cr(SO <sub>3</sub> -salen)-MnMgAl-LDH	41.5	15.8	15.4	11.5	0.3	0	57.8

<sup>a</sup> Reaction conditions: GLY (50 mL, 0.2 mol·L<sup>-1</sup>), 3% H<sub>2</sub>O<sub>2</sub> (30 mL), 0.2 g catalyst, 60 °C, 6 h.

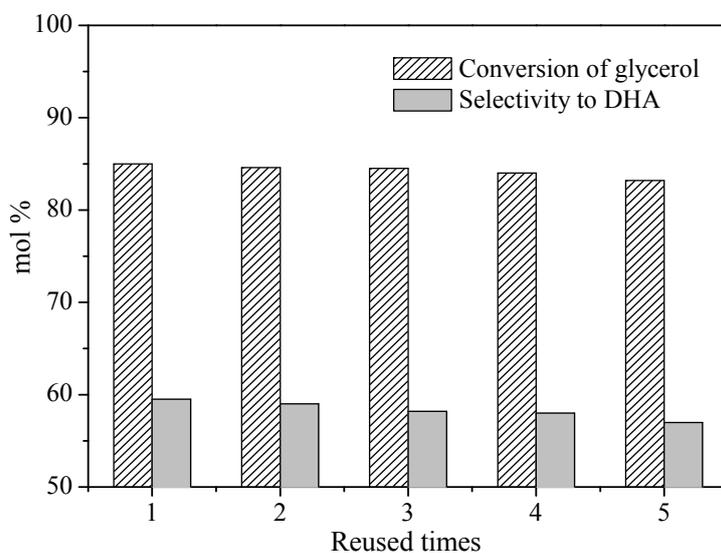
In order to obtain the best catalytic results, the effects of condition parameters on the catalytic performance of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH were investigated with the constant amount of 50 mL glycerol solution (0.2 mol·L<sup>-1</sup>). It was found that the amount of oxidant and catalyst, the reaction time, and temperature all significantly influenced the catalytic performance of LDH-hosted complexes (see Figure 5). Excessive oxidant and catalyst, as well as much too high reaction temperature and long reaction time, went against the selective oxidation of GLY. With the prolonging of the reaction time, the objective product (DHA) was over-oxidized into C1 and C2 products, such as oxallic acid and formic acid. When the reaction ran for 6 h at 60 °C over 0.2 g catalyst with 30 mL 3% H<sub>2</sub>O<sub>2</sub>, the best GLY conversion of 85.5% with 59.3% of the selectivity to DHA was achieved.

In addition, a further study on the stability of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH was also carried out. After the first catalytic run, the catalyst was separated from the reaction solution, washed several times with water to remove any physisorbed molecules, dried and then reused in another five catalytic runs. Figure 6 revealed that the catalyst was still active after being recycling five times. Element analysis disclosed that the reused catalyst held almost the same Cr(III) content (Cr wt. %: 6.35) as fresh catalyst after five uses, which suggested that the Cr(III) leaching was negligible. Thus, the LDH-hosted Cr(III) complex catalysts were stable in the present working conditions.

**Figure 5.** Cont.



**Figure 5.** Effect of the condition parameters on the catalytic performance of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH.



**Figure 6.** Reusability of Cr(SO<sub>3</sub>-salen)-CuMgAl-LDH. Reaction conditions: GLY (50 mL, 0.2 mol·L<sup>-1</sup>), 3% H<sub>2</sub>O<sub>2</sub> 30 mL, catalyst 0.2 g, 60 °C, 6 h.

### 3. Experimental Section

#### 3.1. Catalyst Preparation

##### 3.1.1. Preparation of the Binary LDHs

The binary LDH containing  $C_6H_5COO^-$  anions was prepared by co-precipitation process followed by controlled hydro-thermal treatment. Briefly, a 120 mL aqueous solution A contained 0.09 mol of two-valence metal nitrate and 0.03 mol of three-valence metal nitrate, and a 120 mL aqueous solution B contained 0.06 mol of  $(NH_4)_2CO_3$ . The two solutions were added dropwise with stirring to 120 mL deionized water at room temperature. The addition was performed over 1.0~1.5 h, and the pH value of the obtained mixed solution was maintained close to  $10.0 \pm 0.5$  by addition of appropriate amounts of  $NH_4OH$  (30% ammonia water). The resulting gel-like slurry was moved to autoclaves and hydrothermally treated for 24 h at 100 °C. The as-prepared product was collected after being filtered and washed repeatedly with deionized  $H_2O$  until  $pH = 7$ . Then the precipitate was dried at 100 °C in air for approximately 12 h. Binary LDHs were obtained and denoted as MgAl-LDH, NiAl-LDH, ZnAl-LDH, MgCr-LDH, respectively.

##### 3.1.2. Preparation of the Ternary LDHs

The synthesis process of ternary LDHs was similar to that of binary LDHs except for the dosage of raw materials. Here, solution A contained three kinds of metal nitrate (0.04 mol), and solution B contained 0.06 mol of  $(NH_4)_2CO_3$ . Ternary LDHs were obtained and denoted as MnMgAl-LDH, CoMgAl-LDH, NiMgAl-LDH, CuMgAl-LDH, ZnMgAl-LDH, respectively.

##### 3.1.3. Preparation of the Heterogeneous LDH-Hosted Cr(III) Complex

The synthetic procedures of LDH-hosted Cr(III) complexes had been described in our previous reports in detail [15,18]. Briefly, the salen ligand was synthesized firstly by the condensation reaction of salicylaldehyde and diamine (ethyldiamine) with a salicylaldehyde/amine molar ratio of 2, and then was charged with five times its weight of strong sulfuric acid to synthesize the sulphonato-salen ligand. In virtue of the exchangeable property of the interlayer anions, the sulfonated ligand was sent to ion exchange reaction with the as-prepared LDH containing  $C_6H_5COO^-$  anions in advance. The product was further added to an aqueous solution of  $CrCl_3 \cdot 6H_2O$  with stirring under  $N_2$  atmosphere to obtain the LDH-hosted Cr(III) complex. Here, by changing the LDH carriers, a series of heterogeneous LDH-hosted Cr(III) complexes were prepared successfully and denoted as  $Cr(SO_3\text{-salen})\text{-CuMgAl-LDH}$ ,  $Cr(SO_3\text{-salen})\text{-NiMgAl-LDH}$ ,  $Cr(SO_3\text{-salen})\text{-MnMgAl-LDH}$ , respectively. Their similar structures were illustrated in Scheme 2.

#### 3.2. Characterization

The contents of carbon, hydrogen, nitrogen in samples were measured using a Vario EL analyzer (Elementar, Hannover, DE-NI, Germany). The contents of transition metal were determined by inductively coupled plasma emission spectroscopy (PerkinElmer ICP OPTIMA-3000, Thermo Electron,

Waltham, MA, USA). Surface areas were calculated using BET method on a Micromeritics ASAP-2000 instrument (Micromeritics, Norcross, GA, USA) at  $-196\text{ }^{\circ}\text{C}$ , using static adsorption procedures. Powder XRD patterns were obtained at room temperature on a Rigaku D Max III VC instrument (Rigaku Corporation, Tokyo, JAPAN) using a Cu target with a Ni filter in a  $2\theta$  range of  $5^{\circ}$ – $70^{\circ}$  at 50 kV and 30 mA. FTIR spectra of the samples were recorded on a FT-IR spectrophotometer of Bruker Tensor-27 (Bruker, Ettlingen, DE-BW, Germany) after being pressed into a 13 mm tablet with freshly dried KBr salt. UV-Vis absorption spectra were recorded on a model 2501 PC Shimadzu spectrophotometer (Shimadzu, Kyoto, Japan) (for solid samples, the optical grade  $\text{BaSO}_4$  was used as reference). TEM studies were performed on a JEOL JEM 2100 microscope (Hitachi, Akishima, Japan). SEM studies were carried on a JEOL JSM-7600F microscope (Hitachi, Akishima, Japan).

### 3.3. Catalytic Test

The catalytic oxidation of glycerol was carried out in a three-neck flask (100 mL) under atmospheric pressure. A heat gathering-style magnetism mixer (DF-II) was used for heating and stirring. For each reactor, a certain amount of catalyst was suspended in 50 mL aqueous solution of glycerol ( $0.2\text{ mol}\cdot\text{L}^{-1}$ ). Once the required temperature reached, the required amount of 3%  $\text{H}_2\text{O}_2$  was introduced into the reactor via a mass flow controller. After reaction, catalyst was filtered off, and then was analyzed using an Agilent 1200 series high-performance liquid chromatography (HPLC) equipped with refractive index and Uv-Vis detectors. Product separation in the HPLC was carried out using an Aminex HPX-87H column (Bio-Rad, Philadelphia, PA, USA) operating at  $60\text{ }^{\circ}\text{C}$  with  $0.01\text{ mol/L H}_2\text{SO}_4$  as eluent flowing at  $0.5\text{ mL/min}$ . An injection volume of  $10\text{ }\mu\text{L}$  and a measure time of 30 min were adjusted. The retention times and calibration curves were found using known concentrations of products. During the oxidation reaction, gas in the effluent was collected and analyzed by a BALZERS OMNISTAR QMS200 mass spectrometer (Oerlikon Balzers, Erlenstrasse, Brügg, Switzerland).

## 4. Conclusions

LDH-hosted Cr(III) complex was an efficient catalyst for the catalytic oxidation of GLY to DHA using 3%  $\text{H}_2\text{O}_2$  as oxidant. Additionally, the element composition of LDH plates was found to significantly influence the catalytic performance of LDH-hosted complex catalysts. Among them,  $\text{Cr}(\text{SO}_3\text{-salen})\text{-CuMgAl-LDH}$  exhibited excellent catalytic performance due to the synergistic effect of active Cu species, and the weak base environment in LDH carriers and Cr(III) complex. When the reaction was performed with  $0.2\text{ g}$  catalyst and  $30\text{ mL}$  3%  $\text{H}_2\text{O}_2$  at  $60\text{ }^{\circ}\text{C}$  for 6 h, the optimum glycerol conversion reached 85.5% with 59.3% of the selectivity to DHA. Moreover, the catalysts exhibited excellent stability in the present working condition, and could be recycled at least five times.

## Acknowledgments

The authors acknowledge the financial supports from the National Natural Science Foundation of China (21003073, 21203093), the Natural Science Foundation of Jiangsu Province (BK20141388), the Qing Lan Project of Jiangsu Province and the Academic Talents Training Project of Nanjing Institute of Technology.

## Author Contributions

W.X.L. conceived and designed the experiments; W.G.D. analyzed the data and wrote the paper; J.T.N. and L.Q.B. performed the experiments.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Shul'pin, G.B.; Kozlov, Y.N.; Shul'pina, L.S.; Strelkova, T.V.; Mandelli, D. Oxidation of reactive alcohols with hydrogen peroxide catalyzed by manganese complexes. *Catal. Lett.* **2010**, *138*, 193–204.
2. Sankar, M.; Dimitratos, N.; Knight, D.W.; Carley, A.F.; Tiruvalam, R.; Kiely, C.J.; Thomas, D.; Hutchings, G.J. Oxidation of glycerol to glycolate by using supported gold and palladium nanoparticles. *ChemSusChem* **2009**, *2*, 1145–1151.
3. Prati, L.; Spontoni, P.; Gaiassi, A. From renewable to fine chemicals through selective oxidation: The case of glycerol. *Top. Catal.* **2009**, *52*, 288–296.
4. Zhou, C.H.; Beltramini, J.N.; Lin, C.X.; Xu, Z.P.; Lu, G.Q.; Tanksale, A. Selective oxidation of biorenewable glycerol with molecular oxygen over Cu-containing layered double hydroxide-based catalysts. *Catal. Sci. Technol.* **2011**, *1*, 111–122.
5. Katryniok, B.; Kimura, J.; Skrzyńska, E.; Girardon, J.-S.; Fongarland, P.; Capron, M.; Ducoulombier, R.; Mimura, N.; Paul, S.; Dumeignil, F. Selective catalytic oxidation of glycerol: Perspectives for high value chemicals. *Green Chem.* **2011**, *13*, 1960–1979.
6. McMorn, P.; Roberts, G.; Hutchings, G.J. Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts. *Catal. Lett.* **1999**, *63*, 193–197.
7. Prati, L.; Villa, A.; Chan-Thaw, C.E.; Arrigo, R.; Wang, D.; Su, D.S. Gold catalyzed liquid phase oxidation of alcohol: The issue of selectivity. *Faraday Discuss.* **2011**, *152*, 353–365.
8. Tsuji, A.; Rao, K.T.V.; Nishimura, S.; Takagaki, A.; Ebitani, K. Selective oxidation of glycerol by using a hydrotalcite-supported platinum catalyst under atmospheric oxygen pressure in water. *ChemSusChem* **2011**, *4*, 542–548.
9. Wang, F.F.; Shao, S.; Liu, C.L.; Xu, C.L.; Yang, R.Z.; Dong, W.S. Selective oxidation of glycerol over Pt supported on mesoporous carbon nitride in base-free aqueous solution. *Chem. Eng. J.* **2015**, *264*, 336–343.
10. Zhang, M.Y.; Nie, R.F.; Wang, L.; Shi, J.J.; Du, W.C.; Hou, Z.Y. Selective oxidation of glycerol over carbon nanofibers supported Pt catalysts in a base-free aqueous solution. *Catal. Commun.* **2015**, *59*, 5–9.
11. Zope, B.N.; Hibbitts, D.D.; Neurock, M.; Davis, R.J. Reactivity of the gold/water interface during selective oxidation catalysis. *Science* **2010**, *330*, 74–77.
12. Kapkowski, M.; Bartczak, P.; Korzec, M.; Sitko, R.; Szade, J.; Balin, K.; Lelatko, J.; Polanski, J. SiO<sub>2</sub>-, Cu-, and Ni-supported Au nanoparticles for selective glycerol oxidation in the liquid phase. *J. Catal.* **2014**, *319*, 110–118.

13. Skrzyńska, E.; Ftouni, J.; Mamede, A.S.; Addad, A.; Trentesaux, M.; Girardon, J.S.; Capron, M.; Dumeignil, F. Glycerol oxidation over gold supported catalysts—“Two faces” of sulphur based anchoring agent. *J. Mol. Catal. A* **2014**, *382*, 71–78.
14. Oliveira, L.C.A.; Portilho, M.F.; Silva, A.C.; Taroco, H.A.; Souza, P.P. Modified niobia as a bifunctional catalyst for simultaneous dehydration and oxidation of glycerol. *Appl. Catal. B* **2012**, *117–118*, 29–35.
15. Wang, X.L.; Wu, G.D.; Wang, F.; Ding, K.Q.; Zhang, F.; Liu, X.F.; Xue, Y.B. Base-free selective oxidation of glycerol with 3% H<sub>2</sub>O<sub>2</sub> catalyzed by sulphonato-salen-chromium (III) intercalated LDH. *Catal. Commun.* **2012**, *28*, 73–76.
16. Crotti, C.; Farnetti, E. Selective oxidation of glycerol catalyzed by iron complexes. *J. Mol. Catal. A* **2015**, *396*, 353–359.
17. Oliveira, V.L.; Morais, C.; Servat, K.; Napporn, T.W.; Tremiliosi-Filho, G.; Kokoh, K.B. Glycerol oxidation on nickel based nanocatalysts in alkaline medium—Identification of the reaction products. *J. Electroanal. Chem.* **2013**, *703*, 56–62.
18. Wu, G.D.; Wang, X.L.; Li, J.P.; Zhao, N.; Wei, W.; Sun, Y.H. A new route to synthesis of sulphonato-salen-chromium (III) hydrotalcites: Highly selective catalysts for oxidation of benzyl alcohol to benzaldehyde. *Catal. Today* **2008**, *131*, 402–407.
19. Srinivasan, K.; Kochi, J.K. Synthesis and molecular structure of oxochromium (V) cations. coordination with donor ligands. *Inorg. Chem.* **1985**, *24*, 4671–4679.
20. Choudary, B.M.; Ramani, T.; Maheswaran, H.; Prashant, L.; Ranganath, K.V.S.; Kumarb, K.V. Catalytic asymmetric epoxidation of unfunctionalised olefins using silica, LDH and resin-supported sulfonato-Mn (salen) complex. *Adv. Synth. Catal.* **2006**, *348*, 493–498.
21. 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* **2006**, *249*, 103–110.
22. Kingma, I.E.; Wiersma, M.; van der Baan, J.L.; Balt, S.; Bickelheanpt, F.; de Bolster, M.W.G.; Klumpp, G.W.; Spek, A.L. Intramolecular alkoxyco-baltation: A novel route to the cobalt-carbon bond in a coenzyme B12 model. *Chem. Commun.* **1993**, doi:10.1039/C39930000832.
23. Mukherjee, S.; Samanta, S.; Roy, B.C.; Bhaumik, A. Efficient allylic oxidation of cyclohexene catalyzed by immobilized Schiff base complex using peroxides as oxidants. *Appl. Catal. A* **2006**, *301*, 79–88.
24. Cantrell, D.G.; Gillie, L.J.; Lee, A.F.; Wilson, K. Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. *Appl. Catal. A* **2005**, *287*, 183–190.
25. Zhou, H.; Zhuo, G.L.; Jiang, X.Z. Heck reaction catalyzed by Pd supported on LDH-F hydrotalcite. *J. Mol. Catal. A* **2006**, *248*, 26–31.
26. Cavani, F.; Trifiro, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today* **1991**, *11*, 173–301.