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A new route to synthesis of sulphonato-salen-chromium(III) hydrotalcites: Highly selective catalysts for oxidation of benzyl alcohol to benzaldehyde

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Abstract

The Mg–Al layered-double hydroxides (LDHs) intercalated by three kinds of sulphonato-salen-chromium(III) complexes were prepared and characterized by FTIR, UV–vis, XRD and elemental analysis. It was found that the homogeneous complexes were successfully intercalated into the LDH interlayer via the method of anion exchange followed by coordination with chromium(III) chloride. And the resulting LDH hosted chromium complexes were shown to be effective heterogeneous catalysts for the solvent-free oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) using 30% H_2O_2 as oxidant. Furthermore, owing to the different local environment of the central metal ion chromium(III), the catalyst with the backbone of o-C_6H_4 displayed the highest catalytic performance followed by the $NH(CH_2CH_2)_2$ with the $(CH_2)_2$ showing the lowest BzH yield. In addition, a tentative mechanism was also discussed.

Keywords: Layered-double hydroxide; Schiff base; Anion exchange; Oxidation; Benzyl alcohol; Benzaldehyde

1. Introduction

BzH is an important intermediate for the perfumery, pharmaceutical, dyestuff and agrochemical. It was mainly produced by hydrolysis of benzyl chloride and also as a byproduct in the liquid phase oxidation of toluene to benzoic acid [1]. In the former process, the BzH product contained the traces of chlorine while the selectivity towards BzH was very poor in the latter process. Owing to the practical requirement of chlorine-free BzH in the perfumery and pharmaceutical industries, the oxidation of BzOH to BzH has been extensively investigated in the past [2–6]. But the development of effective (‘‘green’’) catalytic systems that use clean, cheap oxidants such as air, molecular oxygen or H_2O_2 in this oxidation is still an important challenge [7–12], and aerobic oxidation is often difficult to control and sometimes results in combustion [13,14]. Therefore, the design of an efficient catalyst and the choice of appropriate catalytic oxidation process are the keys to realizing an ideal oxidation procedure.

Transition metal Schiff base complexes-catalyzed oxidation of alcohols in resemblance of enzymatic catalysis was eye-catching especially for their more accessible synthesis conditions and versatile coordination structures, and various transition metal complexes have been reported [15–19]. However, such homogeneous complexes suffered from the drawbacks of poor catalyst recovery and product separation [20]. Thus, many groups have tried to immobilize Schiff base complexes on various supports. Li and coworkers reported that a chiral salen-Mn(III) complex immobilized on MCM-41 showed high catalytic performance in the α-methylstyrene epoxidation [21,22]. Kureshy et al. immobilized another chiral salen-Mn(III) complex between the layers of a montmorillonite clay, and the resulting heterogenised complex was effective catalyst in the enantioselective epoxidation of alkene. In recent years, LDH was considered as an effective support due to the layered structure as well as the high maximum exchange capacity. Both the Anderson’s and Choudary’s groups had

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successfully intercalated the sulphonato-Mn(salen) complexes into the interlayer of hydrotalcites [23–27]. It was found that the LDH support could overcome the Mn leaching problem [23], and the catalytic performance of the LDH hosted complexes was largely independent of the central metal ion, suggesting that the local environment of the central metal ion was of great importance [24–27]. Furthermore, it was well known that LDH had the inherent base and the water-resistant structure, which would favor improving the oxidation efficiency of H_2O_2 in liquid oxidation. Thus, in the present paper, we reported a new route to synthesis of Mg–Al LDH hosted sulphonato-salen-chromium(III) complexes as well as their actions as heterogeneous catalysts in the solvent-free selective oxidation of benzyl alcohol to benzaldehyde using 30% H_2O_2 as oxidant.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of the LDH host

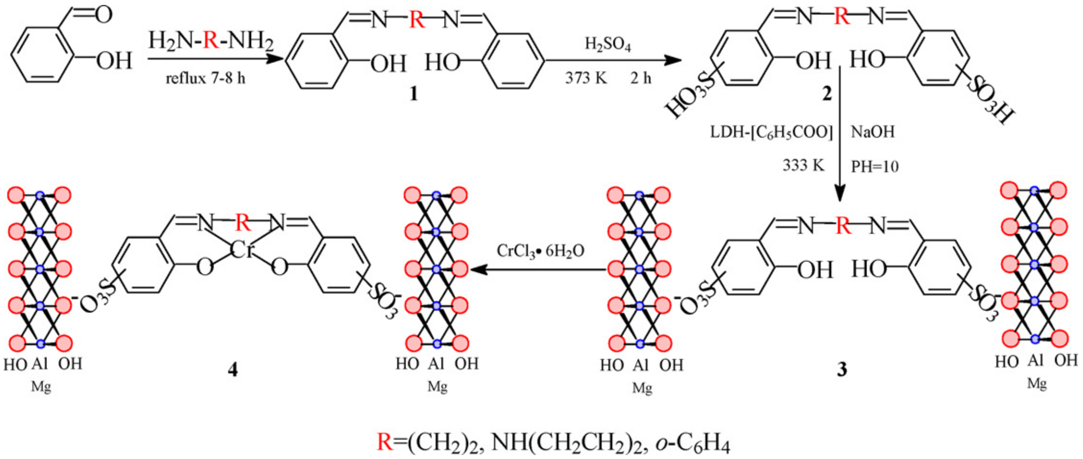
The Mg–Al LDH containing $C_6H_5COO^-$ anions (LDH–[C_6H_5COO]) was prepared by coprecipitation method followed by controlled hydrothermal treatment. Briefly, a solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.09 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.03 mol) in deioned decarbonated (DD) water (120 mL) was added dropwise with vigorous stirring to a solution of C_6H_5COOH (0.06 mol) and NaOH (0.30 mol) in DD water (120 mL) at room temperature under N_2 atmosphere. The resulting gel-like slurry was hydrothermally treated at 373 K for 24 h, then filtered and washed with DD water until pH 7. The precipitate was dried at 373 K for 12 h and then LDH–[C_6H_5COO] was obtained.

2.1.2. Preparation of the heterogeneous LDH–[Cr(SO_3-salen)] 4

The Mg–Al LDH hosted sulphonato-salen-chromium(III) complexes **4** LDH–[Cr(SO_3-salen)] were prepared by the synthetic strategy shown in Scheme 1. As reported in literature [28], the salen ligand was prepared firstly by the condensation of salicylaldehyde and diamines (ethyldiamine, diethyltriamine or *o*-phenylenediamine) with a salicylaldehyde/amine molar ratio of 2. In a typical synthesis, diamine (0.02 mol) was suspended in 60 mL absolute ethanol. Then salicylaldehyde (0.04 mol) dissolved in 60 mL absolute ethanol was added dropwise to the suspension with vigorous stirring. The resulting mixture was refluxed for 7–8 h. In this way, three bright yellow salen ligands **1** were obtained. Then the as-prepared **1** was charged in a 120 mL round-bottomed flask containing five times its weight of concentrated sulfuric acid. This mixed solution was heated at 373 K for 2 h. After cooling by ice water, the solution was slowly added to anhydrous alcohol (500 mL) with vigorous stirring to precipitate the pale yellow crystal. The crystal was further filtered out, washed and soxhlet extracted for 7–8 h with anhydrous alcohol and dried in air. And then the sulphonate salen ligands **2** were obtained, which was the mixture of 3-sulphonate salen ligand (*ortho* to the OH) and 5-sulphonate salen ligand (*para* to the OH). The obtained **2** was then dissolved in 120 mL DD water at 333 K and the pH value was modified to about 10.0 by adding appropriate amounts of NaOH. And the as-prepared LDH–[C_6H_5COO] (0.01 mol, 3.7 g) was added to the above solution and the resultant mixture was stirring for 24 h at 333 K under N_2 atmosphere. The product was filtered and washed with DD water and dried at 333 K for 12 h, affording the products **3** of LDH intercalated by the sulphonic salen ligands. Then **3** was added to an aqueous solution (100 mL) of $CrCl_3 \cdot 6H_2O$ (0.008 mol) with stirring under N_2 atmosphere. After refluxing for 1 h, the mixture was cooled and filtered under reduced pressure. The solid product was washed with DD water and dried at 333 K for 12 h, and then LDH–[Cr(SO_3-salen)] **4** was obtained.

2.1.3. Preparation of the disodium salt of chromium salen complexes Na_2[Cr(SO_3-salen)]

To allow for the direct comparison with LDH–[Cr(SO_3-salen)], the homogeneous disodium salt of sulphonato-salen-chromium(III) complexes Na_2[Cr(SO_3-salen)] were also prepared. Typically, the as-prepared pale yellow crystal of sulphonic salen ligand **2** (0.02 mol) was dissolved in 120 mL DD water at 333 K and the pH value was modified to about 7.0



Scheme 1. Preparation of MgAl–LDH–[Cr(SO_3-salen)].

by adding appropriate amounts of NaOH prior to the addition of $CrCl_3 \cdot 6H_2O$ (0.024 mol). After refluxing for 6 h, the mixture was cooled and filtered. The collected solid was washed with absolute ethanol, dried in air, and recrystallized from absolute ethanol.

2.2. Characterization

The Fourier transform infrared (FTIR) spectroscopy results of the samples were recorded on a Shimadzu (model 8201 PC) spectrophotometer after being pressed into 13 mm discs with freshly dried KBr salt. Visible-Ultra-violet-Spectrophotometry (UV–vis) was recorded on a Shimadzu (model 2501 PC) spectrophotometer, and the optical grade $BaSO_4$ was used as reference. Powder X-ray diffraction (XRD) experiments of samples were carried out on a Rigaku Miniflex diffractometer using a Cu target with a Ni filter. And the X-ray gun was operated at 50 kV and 30 mA, using a scan speed rate 0.2° min^{-1}. The contents of carbon, hydrogen, nitrogen and sulfur of all samples were determined using a Vario EL analyzer. The contents of magnesium, aluminum and chromium were measured by inductively coupled plasma (ICP) emission spectroscopy (Perkin-Elmer ICP OPTIMA-3000).

2.3. Catalytic test

The oxidation of BzOH was carried out in a 100 mL Teflon-lined and magnetically stirred autoclave. Typically, 0.3 g heterogeneous catalyst or 1 mol% of homogeneous complex (relative to H_2O_2) and 5.41 g BzOH were introduced and stirred for about 10 min, and then 13.6 mL 30% H_2O_2 was added. The autoclave was heated to 323 K. After the reaction run for 2 h, the products were analyzed using a gas chromatograph equipped with a capillary 30 m HP-5 column and an FID detector after centrifugal separation from catalysts. H_2O_2 consumption was determined by the iodometric titration after the reactions.

3. Results and discussion

3.1. Intercalation and structure

The FTIR spectra of LDH-[C_6H_5COO], **2** ($R{=}CH_2CH_2$) and **4** ($R{=}CH_2CH_2$, $NH(CH_2CH_2)_2$ and o-C_6H_4) are typically illustrated in Fig. 1. It could be seen that **2** ($R{=}CH_2CH_2$) exhibited characteristic bands at 1110 and 1035 cm^{-1} due to the anti-symmetric and symmetric stretching modes of the SO_3^- moiety, together with the bands at 1636 and 1520 cm^{-1} ascribed to υ(CH=N) and υ(C=O), respectively [23–27], confirming that **2** ($R{=}CH_2CH_2$) was successfully sulphonated from salen ligand **1** with the concentrated sulfuric acid. For **4** ($R{=}CH_2CH_2$), the characteristic bands of the SO_3^- moiety were also found at 1112 and 1034 cm^{-1} with marginal shift in comparison with the free sulphonic salen ligand **2**. Furthermore, **4** ($R{=}CH_2CH_2$) not only showed the bands at 1621 cm^{-1} υ(CH=N) and 1529 cm^{-1} υ(C–O) with red shift (15 cm^{-1}) and blue shift (9 cm^{-1}) with respect to the free sulphonic salen ligand **2**, but also displayed the bands at 597 and 418 cm^{-1} associated with υ(Cr–O) and υ(Cr–N). This indicated that chromium(III) was bonded through the two N and O donor atoms of the ligand as a tetradentate ONNO functionality [23–27]. The above characteristic bands were not present in the spectrum of LDH–[C_6H_5COO], implying that the sulphonato-salen-chromium(III) anions [Cr(SO_3-salen)]$^{2-}$, were successfully intercalated into the Mg–Al LDH interlayer through the method of anion exchange followed by coordination with chromium(III) chloride. At the same time, for **4** with the diimine backbones of $NH(CH_2CH_2)_2$ and o-C_6H_4, the characteristic bands of the SO_3^- moiety and the tetradentate ONNO functionality were both present only with slight shift (see Fig. 1 and Table 1), suggesting that the LDH–[Cr(SO_3-salen)] with this two backbones had also been successfully prepared by the same method.

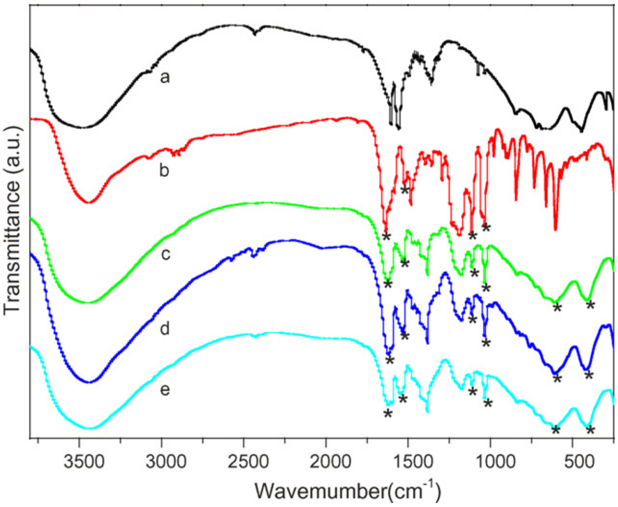


Fig. 1. FTIR spectra of the samples: (a) LDH–[C_6H_5COO]; (b) 2 ($R{=}CH_2CH_2$); (c) **4** ($R{=}CH_2CH_2$); (d) **4** ($R{=}NH(CH_2CH_2)_2$); (e) **4** ($R{=}o$-C_6H_4).

Fig. 2 displays the UV–vis spectra of the as-prepared samples. The characteristic peaks of LDH–[C_6H_5COO] were found at about 221 and 272 nm, which were associated with the π–π^* transitions of aromatic rings. Simultaneously, **2** ($R{=}CH_2CH_2$) displayed two characteristic bands at about 259 and 351 nm, which could be assigned to the π–π^* transitions of aromatic rings and the C=N groups, respectively [23–27]. This indicated that free sulphonic salen ligand **2** ($R{=}CH_2CH_2$) had been successfully prepared. However, after anion exchange and coordination with chromium(III), the peaks of **2** ($R{=}CH_2CH_2$) almost disappeared or more weakened, while a new peak at about 410 nm typical of the ligand to metal charge transfer and a broad band at about 580 nm associated with d–d transition appeared in **4** ($R{=}CH_2CH_2$), confirming that the [Cr(SO_3-salen)]$^{2-}$ anions were successfully intercalated into the LDH interlayer. Similarly, when R was $NH(CH_2CH_2)_2$ and o-C_6H_4, the typical ligand–metal bands were observed at about 396, 446 nm, respectively, while the d–d transitions also appeared at about 580 nm independent of the diimine backbones. This further confirmed that the three LDH hosted chromium complexes all had been successfully prepared.

Table 1
Results of elemental analysis, FTIR and UV–vis spectra of samples

Samples	Elemental analysis data (wt%)							C/N[a]	Spectroscopic data	
	C	H	N	S	Cr	Mg	Al		FTIR (cm^{-1})	λ_{max} (nm)
LDH–[C_6H_5COO]	20.24	4.23	–	–	–	20.36	6.52	–	1600, 1550	221, 272
2 (R=CH_2CH_2)	44.85	3.77	6.54	14.97	–	–	–	8.05 (8.00)[b]	1636, 1520, 1110, 1035	259, 351
4 (R=CH_2CH_2)	25.15	2.89	3.66	8.39	6.80	11.00	3.53	8.02 (8.00)[b]	1621, 1529, 1112, 1034, 597, 418	270, 410, 580
4 NH(CH_2CH_2)$_2$	25.95	3.45	5.04	7.70	6.24	10.94	3.24	6.00 (6.00)[b]	1617, 1527, 1107, 1032, 612, 419	270, 396, 580
4 (*o*-C_6H_4)	29.40	2.72	3.42	7.84	6.36	10.66	3.30	10.03 (10.00)[b]	1624, 1541, 1114, 1039, 605, 412	280, 446, 580

[a] The molar ratio of C to N.
[b] The theoretical value calculated from the framework in Scheme 1.

The XRD patterns of LDH–[C_6H_5COO] and **4** (R=CH_2CH_2) are typically shown in Fig. 3, and they almost showed the same pattern characteristic of LDH [29]. It was well known that the LDH characteristics could be depicted by two important cell parameters of *c* ($3d_{003}$) and *a* ($2d_{110}$). The parameter *c* was related to the basal spacing, which depended on the hydrated anion size and electrostatic force in the hydrotalcite-like interlayer. The parameter *a* was related to the atomic distributed density in (1 1 0) platelet and depended on the Mg/Al molar ratio [30,31]. In comparison with LDH–[C_6H_5COO] (d_{003} $\approx$15.82 Å, $d_{110} \approx 1.49$ Å) [26,27], **4** (R=CH_2CH_2) showed an increase in d_{003} (19.58 Å) without the change in d_{110} (1.49 Å). That is to say, the *c* value of **4** (R=CH_2CH_2) increased but the *a* value kept invariable compared to the two parameters of LDH–[C_6H_5COO]. The increase in *c* value displayed that the basal spacing of **4** (R=CH_2CH_2) obviously increased in comparison with that of LDH–[C_6H_5COO], which strongly suggested the [Cr(SO_3-salen)]$^{2-}$ anions were successfully intercalated into the Mg–Al LDH interlayer. The unaltered *a* value indicated that **4** (R=CH_2CH_2) and LDH–[C_6H_5COO] still kept the same Mg/Al molar ratio and no loss of Mg^{2+} and Al^{3+} occurred during the process of anion exchange followed by coordination. Thus, the interaction of sulphonato-salen-chromium(III) anions into the Mg–Al LDH interlayer did not change the hydrotalcite-like structure of LDH host.

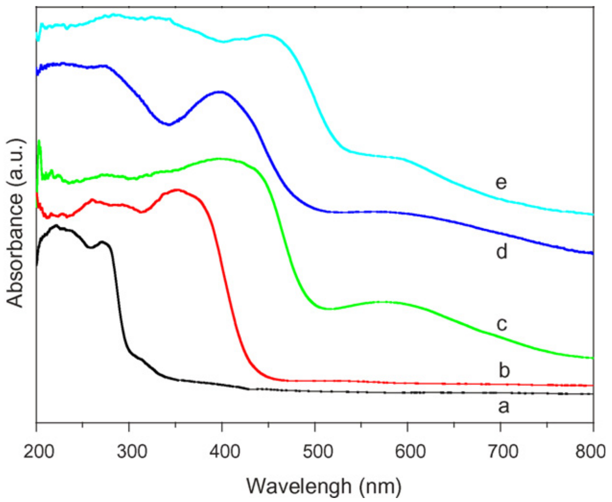


Fig. 2. UV–vis spectra of the samples: (a) LDH–[C_6H_5COO]; (b) 2 (R=CH_2CH_2); (c) **4** (R=CH_2CH_2); (d) **4** (R=NH(CH_2CH_2)$_2$); (e) **4** (R=*o*-C_6H_4).

The results of chemical analysis (see Table 1) revealed that the elemental composition in LDH–[C_6H_5COO] and **4** (R=CH_2CH_2) were in reasonable agreement with the unit formula of $Mg_{3.09}Al_{0.89}(OH)_{7.96}[C_6H_5COO]_{0.89}\cdot 1.5H_2O$ and $Mg_{3.01}Al_{0.87}(OH)_{7.76}[Cr(SO_3\text{-salen})]_{0.87}\cdot 1.3H_2O$, respectively. At the same time, the C/N molar ratios of all LDH hosted chromium complexes were well consistent with the theoretical value calculated from the framework in Scheme 1. This indicated that almost no $C_6H_5COO^-$ anions remained in LDH interlayer, or else the C/N molar ratios of heterogenised complexes should be higher than the expected value. Furthermore, in FTIR spectra of the three LDH hosted chromium complexes, the characteristic bands of $C_6H_5COO^-$ anions (1550 cm^{-1}) no longer appeared, also suggesting that $C_6H_5COO^-$ anions might have been completely exchange out of LDH interlayer. Therefore, LDH–[Cr(SO_3-salen)] could be successfully prepared via the method of anion exchange followed by coordination.

3.2. Local environments and catalytic performance

Without any organic solvent, phase transfer catalyst or additive, the catalytic performance of the so-obtained catalysts was investigated in the selective oxidation of BzOH to BzH with 30% H_2O_2. The results listed in Table 2 showed that no

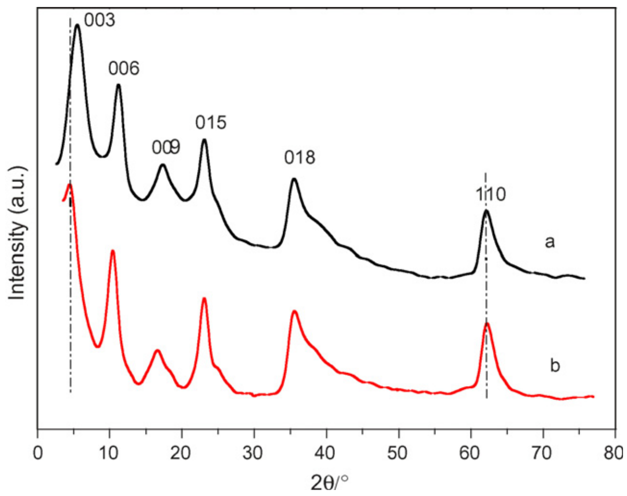


Fig. 3. XRD patterns of the samples: (a) LDH–[C_6H_5COO]; (b) 4 (R=CH_2CH_2).

Table 2
The catalytic activity of different samples*

Catalyst	Conversion (%)		Selectivity (%)		
	H_2O_2	BzOH	Benzaldehyde	Benzoic acid	Benzyl benzoate
Blank	6.3	2.7	65.8	22.4	11.8
$Na_2[Cr(SO_3\text{-salen})]$[a]	40.5	19.5	75.8	14.6	9.6
$Na_2[Cr(SO_3\text{-salen})]$[b]	45.6	25.3	74.6	17.9	7.5
$Na_2[Cr(SO_3\text{-salen})]$[c]	50.2	28.8	77.5	15.6	6.9
LDH–$[C_6H_5COO]$	9.3	3.1	80.2	13.1	6.7
LDH–$[Cr(SO_3\text{-salen})]$[a]	67.5	35.7	100.0	0	0
LDH–$[Cr(SO_3\text{-salen})]$[b]	74.6	52.3	100.0	0	0
LDH–$[Cr(SO_3\text{-salen})]$[c]	88.2	65.8	100.0	0	0

* (a) R=CH_2CH_2; (b) $NH(CH_2CH_2)_2$; (c) R=*o*-C_6H_4.Reaction condition: heterogenised catalysts, 0.3 g or 1 mol% of homogeneous catalyst (relative to BzOH); BzOH, 5.41 g; H_2O_2/BzOH = 2.6/1.0 (molar ratio); Temperature, 323 K; Time, 2 h.

significant amount of BzH was produced in the absence of catalyst and over LDH–$[C_6H_5COO]$. With the homogeneous $Na_2[Cr(SO_3\text{-salen})]$ as catalysts, though the catalytic activity increased to some extent, the selectivity towards BzH was still relatively lower. However, when the reaction was performed over LDH hosted chromium complexes (LDH–$[Cr(SO_3\text{-salen})]$), the BzOH conversion were sharply improved with the concomitant selectivity of 100%, indicating that the synergic effect took place between the $[Cr(SO_3\text{-salen})]^{2-}$ anions and the LDH host. Simultaneously, LDH–$[Cr(SO_3\text{-salen})]$ also exhibited much higher H_2O_2 decomposition activity than $Na_2[Cr(SO_3\text{-salen})]$, which could be reasonably attributed to the introduction of the weak base LDH host (OH^-). It was known that the weak base environment benefited the cleavage of peroxide bond in H_2O_2 due to the formation of H-bonding between the OH^- and the hydrogen atom of H_2O_2, which could significantly improve the oxidation capacity of H_2O_2. This might to some extent afford the much higher catalytic performance over LDH–$[Cr(SO_3\text{-salen})$ than over $Na_2[Cr(SO_3\text{-salen})]$.

Furthermore, LDH–$[Cr(SO_3\text{-salen})]$ with the backbone of *o*-C_6H_4 exhibited the highest catalytic performance among the three heterogenised catalysts (see Table 2). Such a significant difference could be related to the different electronic structures and steric effect of the three backbones [32,33]. With the electron-withdrawing group of *o*-C_6H_4 using as backbone, it linked the two phenyls via the two imines (–C=N–), which contributed to the formation of the π-extended coordination structure. As a result, the electronic density around the central metal ion Cr(III) decreased, and the stability of the heterogenised complex increased significantly, which helped to the formation of active oxochromium intermediate and thus benefited the oxidation. Furthermore, *o*-C_6H_4 was in favor of H_2O_2 touching the catalytic active sites owing to its plane structure, and this also further facilitated the oxidation. On the contrary, the backbones of $NH(CH_2CH_2)_2$ and CH_2CH_2 were both electron-donating groups, which could increase the electronic density around the central metal ion and then went against the formation of oxochromium. Nevertheless, when the $NH(CH_2CH_2)_2$ was used as backbone, the hyperconjugation effect took place between the N of methane amine and the –C–H of azomethine. This decreased the electronic density to some extent, and then the resulting catalyst with backbone of $NH(CH_2CH_2)_2$ showed relatively higher catalytic performance than that with CH_2CH_2 as backbone. Consequently, the catalytic performance of the three heterogenised catalysts decreased in the following sequence of diimine backbones: *o*-$C_6H_4 > NH(CH_2CH_2)_2 > (CH_2)_2$.

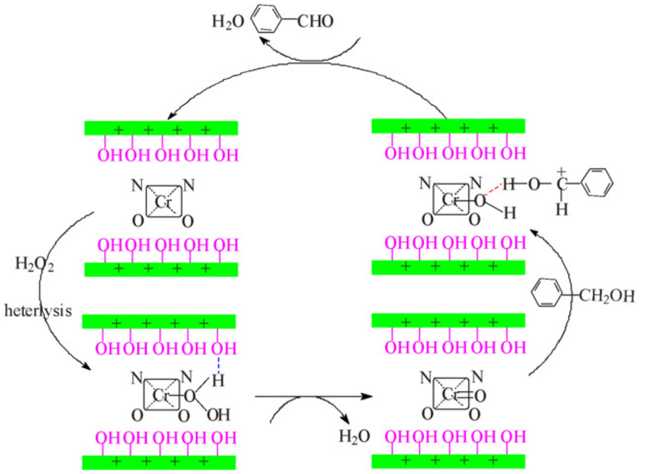
3.3. Possible mechanism

The mechanism of alcohol oxidation by oxometal complexes is attracting continuous interests, and various mechanistic pathways have been reported [34,35]. Relative reasonable mechanisms were the ionic mechanism and the free-radical mechanism. To check the presence of radicals, the following inhibition experiments were designed by the use of three radical scavengers with **4** (R=*o*-C_6H_4) as the representative catalyst. No significant lowering of the conversion of BzOH was observed in the inhibition experiments (see Table 3), suggesting the involvement of ionic mechanism. Furthermore, FTIR spectra of the complexes **4** treated with H_2O_2 displayed bands at 863 cm^{-1} (R=CH_2CH_2), 869 cm^{-1} ($NH(CH_2CH_2)_2$) and 867 cm^{-1} (R=*o*-C_6H_4), typical of known Cr(V)-oxo stretching vibration. These bands were not found in the FTIR spectra of the corresponding untreated complexes, further confirmed that ionic mechanism was more in line with our results [35]. Thus, a possible mechanism of BzOH oxidation over LDH hosted sulphonato-salen-chromium complexes was illustrated in Scheme 2. Namely, the coordinatively unsaturated chromium(III) activated H_2O_2 via heterolytic cleavage of the peroxide

Table 3
Effect of the different radical scavengers on the oxidation of BzOH

Additive	Conversion (%) (BzOH)	Selectivity (%)		
		Benzaldehyde	Benzoic acid	Benzyl benzoate
–	65.8	100.0	0	0
Pyrocatechol	64.8	100.0	0	0
Resorcinol	66.5	98.5	0	1.5
Hydroquinone	64.0	100.0	0	0

Reaction conditions: catalyst of LDH–$[Cr(SO_3\text{-salen})]$ (R=*o*-C_6H_4), 0.3 g; BzOH, 5.41 g; H_2O_2/BzOH = 2.6/1.0 (molar ratio); Temperature, 323 K; Time, 2 h.



Scheme 2. Possible mechanism for the selective oxidation of BzOH over MgAl–LDH–[Cr(SO_3-salen)].

bond, which resulted in the formation of a high-valent oxochromium intermediate. Then the oxochromium intermediate abstracted a hydrogen from BzOH to generate a α-hydroxycarbon cation (H(OH)PhC^+). Simultaneously, this oxochromium intermediate itself was converted into hydroxychromium intermediate, which further reacted with the α-hydroxycarbon cation to produce the product.

4. Conclusions

Three LDH hosted sulphonato-salen-chromium(III) complexes were successfully prepared via the method of anion exchange followed by coordination and exhibited promising catalytic performance towards the selective oxidation of BzOH with 30% H_2O_2. It was found that the electron-withdrawing backbone and the weak base environment of the LDH support both played positive roles in catalytic performance of the LDH hosted chromium complexes. The as-prepared sample with *o*-C_6H_4 as backbone exhibited the highest catalytic performance, and the optimal BzOH conversion could reach 65.8% with 100% of the selectivity to BzH.

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