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Copper Tetrasulfophthalocyanine Intercalated Hydrotalcite as an Efficient Bifunctional Catalyst for the Baeyer–Villiger Oxidation

Weiyou Zhou[1] · Yong Chen[1] · Junfeng Qian[1] · Fu'an Sun[1] · Mingyang He[1] · Qun Chen[1]

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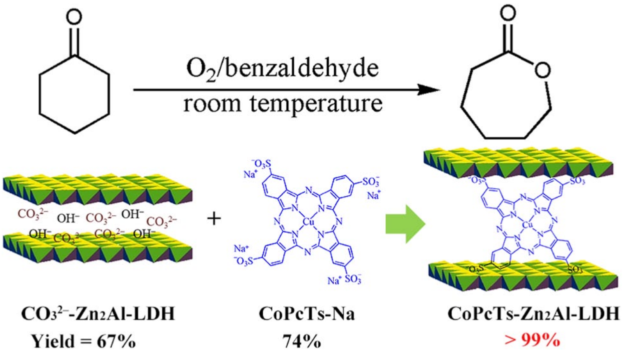
Abstract A heterogeneous bifunctional hybrid catalyst originated from copper tetrasulfophthalocyanine (CuPcTs) and hydrotalcite for Baeyer–Villiger (B-V) oxidation has been prepared and characterized. XRD, FTIR, DR UV-Vis and SEM characterization indicate that CuPcTs molecule has been successfully intercalated into the layer of ZnAl hydrotalcite. And the synthesized hybrid exhibited excellent catalytic activity in the B-V oxidation for various ketones under mild conditions. Its bifunctional role in the reaction through O_2/benzaldehyde has been discussed and verified by controlled experiments. The study indicates that the designed catalyst not only catalyzes the oxidation of benzaldehyde to perbenzoic acid, but also accelerates the transformation of ketone to lactone or ester.

Graphical Abstract



Keywords Hydrotalcite-like compounds · Copper phthalocyanine · Baeyer–Villiger oxidation · Bifunctional catalyst

1 Introduction

The Baeyer–Villiger (B-V) oxidation is an important reaction for directly transforming a ketone to a lactone or ester, and has been widely applied in organic synthesis and fine chemical industries [1–3]. Peroxides, such as persulfuric acid [4], perbenzoic acid [5, 6], *tert*-butylhydroperoxide [7], *m*-chloroperbenzoic acid (*m*-CPBA) and hydrogen peroxide (H_2O_2) [8–11] are commonly used in the reaction. However, these oxidants not only require expensive protection, some of them but also cause a lot of waste material, the O_2/aldehyde oxidation system will be quite attractive from an industrial viewpoint.

Actually, varied materials have been introduced to catalyze the B-V oxidation through O_2/aldehyde, including metallo complexes [12], active carbon [13], transition metal ions or their oxides [14–17], metals supported on various supports [18–20] and hydrotalcites [21, 22], etc. According to the generally accepted reaction scheme for the oxidation system consists of two reaction steps, namely peracid formation from aldehyde and O_2 and the oxidation of the reactant by the peracid [23].

However, most of the reported catalysts could only catalyze one of the two steps. Developing a bifunctional catalyst on the basis of the reaction mechanism, which can catalyze both of the reaction steps, should be very attractive. Kaneda et al. [24] had introduced a transition metal like Fe, which has catalytic activity in the oxidation of aldehyde, into the hydrotalcite structure, and found that the catalytic activities

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✉ Mingyang He
hemy_cczu@126.com

[1] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

of the new catalysts were substantially improved in the B-V oxidation.

On the other hand, metallophthalocyanine, as a biomimetic catalyst for P450, has received considerable attention and exhibited excellent performance in the oxidation of varied substrates using oxygen as the oxidant [25–28]. Therefore, we speculated that the metallophthalocyanine molecule may also exhibit catalytic activity in the first step of B-V oxidation, namely the transformation of benzaldehyde to perbenzoic acid.

On the basis of above analysis, we envisioned that the hybrid formed by intercalating metallophthalocyanine into hydrotalcite (LDH) may accelerate both of the steps in the B-V oxidation by O_2/aldehyde, since hydrotalcite has been generally proved to be an effective catalyst for the second step [22]. In addition, the intercalated materials would also afford a heterogeneous catalyst for metallophthalocyanine and increase its durability in reactions [18], because the deactivation of active sites is always caused by oxidative decomposition and aggregation of metallo complex by π–π interaction in homogeneous system.

In our previous research, we have developed a cobalt porphyrin intercalated hydrotalcite hybrid for the reaction, and excellent catalytic activity in the B-V oxidation of varied ketones was observed [29]. In the present study, Copper tetrasulfophthalocyanine anion (CuPcTs), which is probably more accessible than metalloporphyrins from a preparation point of view, intercalated ZnAl hydrotalcite has been prepared as a bifunctional catalyst for the aerobic B-V oxidation under milder conditions.

2 Experimental

All reagents and solvents were of analytical grade and were obtained commercially. CuPcTs was prepared and purified as reported [30]. No impurities were found in the cyclohexanone by GC-MS analysis before use.

2.1 Synthesis of CuPcTs-Zn_2Al-LDH

Typically, the samples were obtained by the coprecipitation of metal nitrates and sodium CuPcTs. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1.67 g, 0.0056 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (1.05 g, 0.0028 mol) was dissolved in 50 mL of deionized water. The aqueous solution was slowly added with mechanic stirring to 10 mL of distillated water at 25 °C with sodium CuPcTs (1.51 g, 1.54×10^{-3} mol); pH = 7.5 was maintained by the continuous addition of 0.1 mol L^{-1} NaOH. The resulting suspension was stirred for 24 h at 80 °C under N_2 atmosphere. The product was filtered, washed with distilled water at 80 °C and finally dried at room temperature. According to ICP analysis, the amounts of immobilized CuPcTs into ZnAl hydrotalcite was 22.7 % by weight; the Zn/Al atomic ratio was estimated to 2.0, which is consistent with the expected composition for the host structure.

2.2 Characterization of Catalysts

The compositions of samples were analyzed by ICP using a Varian Vista-AX device. The XRD patterns were recorded on a Rigaku D/max 2500 PC X-ray generator with Cu-Kα (1.5402 Å) radiation at 10 min^{-1}. Basal spacing distances were determined from the position of the d(003) reflection. FTIR spectra of samples were recorded using KBr disks on a Nicolet PROTÉGÉ 460 FTIR spectrometer. For the SEM study of the LDHs, a JEOL JSM-6360LA scanning electron microscope was used. Diffuse reflectance ultraviolet visible spectroscopy (DR UV-Vis) was analyzed on a Perkin-Elmer Instruments Lambda 35.

2.3 Catalytic B-V Oxidation

The catalytic oxidation of ketone was carried out in a round-bottom flask of 25 mL volume equipped with magnetic stirrer. In the typical experiment, the flask was charged with substrate (2 mmol), CuPcTs-Zn_2Al-LDH (8.0 mg), dichloroethane (10 mL), benzaldehyde (5 mmol), naphthalene (inert internal standard, 0.3 mmol) and then the mixture was stirred at room temperature. Dioxygen was bubbled through the solution (10 mL min^{-1}). We sampled during the reaction and the products were analyzed by GC-FID and GC-MS analysis.

3 Results and Discussion

3.1 Characterization of CuPcTs-Zn_2Al-LDH

From the literature [31], coprecipitation at constant pH generally is a better method for preparing LDHs than directly anion-exchange procedure. The X-ray powder diffraction patterns (XRD) is always used to identify the structure of hydrotalcites, and Fig. 1 shows the XRD patterns of CuPcTs-Zn_2Al-LDH and CO_3^{2-}-Zn_2Al-LDH as comparison. The pattern of CO_3^{2-}-Zn_2Al-LDH sample shows common features with reflections located at the angles typical of a hydrotalcite-like phase: sharp and symmetrical for (003), (006), (110) and (113), and broad and asymmetrical for (009), (015) and (018), respectively [32, 33]. In relation to CuPcTs-Zn_2Al-LDH sample containing CuPcTs intercalated in the layers, its XRD pattern is very different from the CO_3^{2-}-Zn_2Al-LDH, but similar to that of CoTSPP-Zn_2Al-LDH [29]: a lower crystallinity and new peaks observed in the 2θ range 2.5–30° (Fig. 1).

Because of the rhombohedral packing of the LDH unit cell [34], the (hkl) reflections along the c axis (003) will

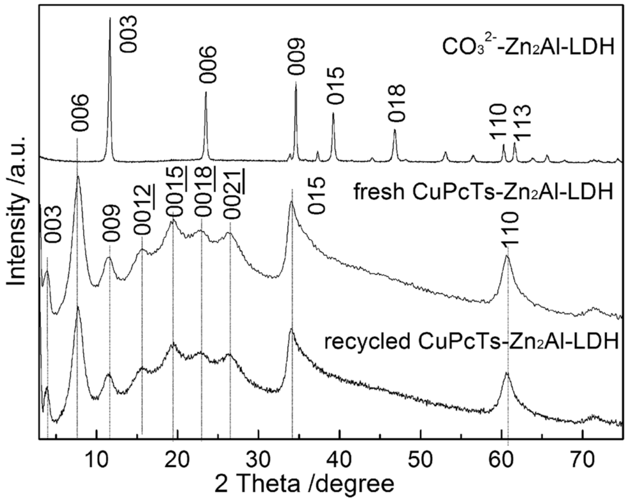


Fig. 1 XRD patterns of CO_3^{2-}-Zn_2Al-LDH, CuPcTs-Zn_2Al-LDH and recycled CuPcTs-Zn_2Al-LDH

increase with the ABCABC-type stacking. The (00l) peaks are shifted to lower 2θ values upon incorporation of the large CuPcTs anion, compared to the pattern of LDH with the smaller interlayer CO_3^{2-} anion. These results indicate a hydrotalcite structure was formed, which are consistent with that reported by Carrado [31] and Abellán [35], etc. All the diffractions can be assigned to pure phases of the hybrid and no impurities such as $Zn(OH)_2$, $Al(OH)_3$ or CO_3^{2-}-Zn_2Al-LDH were observed [36], indicating the high affinity of anionic phthalocyanine toward the hydroxide layers.

The basal spacing distance of LDHs are actually dependent on the size of anions and their orientation between the layers. By calculating from the reflection (003), a distance of 7.5 Å was obtained for CO_3^{2-}-Zn_2Al-LDHs, which is typical for hydrotalcite-like materials containing carbonate anions [37]. Considering the same crystalline system used to assign the LDH peaks, one could calculate the hybrid LDH's interlayer distance of 22.6 Å, much higher than that obtained for the general inorganic anions such as CO_3^{2-}. Therefore, the interlayer distance of intercalated material undergoes a large increase from 7.5 to 22.6 Å following the intercalation process.

The interlayer space available for intercalated phthalocyanine anions can be estimated similarly to hybrid LDH by subtracting a thickness of the hydroxide layer (i.e. 4.80 Å) from the basal spacing supposing that anionic substituents are arranged between the zinc tetrahedra [22]. The obtained gallery height of about 17.8 Å is comparable with the calculated dimensions of the copper phthalocyanine molecular plane (ca. 18 × 18 × 5.5 Å) [31]. This spacing allows CuPcTs to have its long axis oriented nearly perpendicular to the clay layers, in accordance with that of CuPcTs-Mg_2Al-LDH [34].

Fourier transform infrared spectrometer (FT-IR) was also used to characterize the CuPcTs-Zn_2Al-LDH hybrid. Figure 2 shows that the characteristic vibration modes associated with the copper phthalocyanine are present in the intercalated hybrid between 600 and 800 and 1000–1500 cm^{-1} [35, 39]. The sharp stronger band at 1384 cm^{-1} corresponding to the carbonate anion[24] in the Zn_2Al hydrotalcites interlayers disappears in the hybrid, indicating that CuPcTs has been intercalated intact into the LDH, and no CO_3^{2-}-Zn_2Al-LDH formed as impurity during the precipitation procedure.

The absorption spectrum of pure solid CuPcTs and CuPcTs-Zn_2Al-LDH both display the Soret band at 352 nm and two Q bands at about 620 and 680 nm, while CO_3^{2-}-Zn_2Al-LDH does not exhibit any absorption in these ranges (Fig. 2). The results further confirm that CuPcTs has been intercalated into the interlayer of LDH.

The crystal morphologies of the prepared samples were investigated with scanning electron microscopy (SEM). The SEM images in Fig. 3 show that both of CO_3^{2-}-Zn_2Al-LDH and CuPcTs-Zn_2Al-LDH formed plate-like agglomerated crystals, representing the character of layered materials [41, 42].

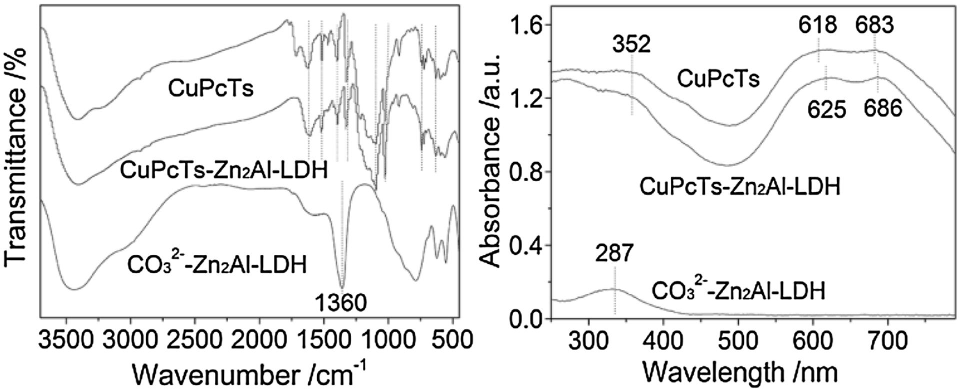


Fig. 2 FTIR and DR UV-Vis spectra of CO_3^{2-}-Zn_2Al-LDH, CuPcTs-Zn_2Al-LDH and CuPcTs

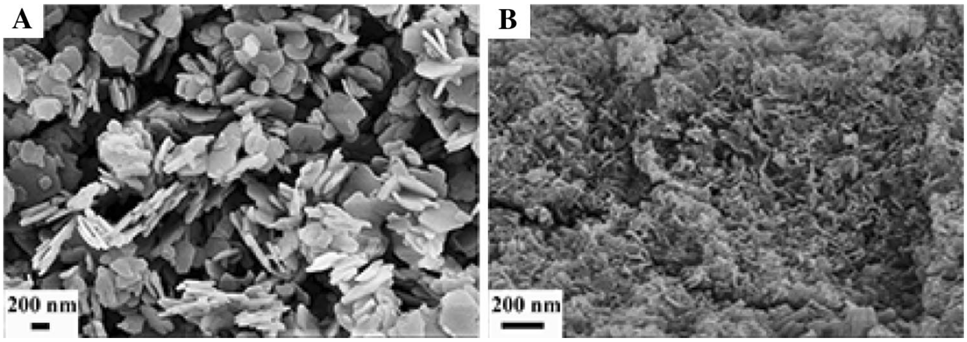


Fig. 3 SEM images of CO_3^{2-}-Zn_2Al-LDH (**a**) and CuTSPP-Zn_2Al-LDH (**b**)

In summary, these characterizations presented above show that CuPcTs has been successfully intercalated into the interlayer of ZnAl hydrotalcite and plate-like agglomerated crystals formed. And the inductively coupled plasma-optical emission spectrometry (ICP-OES) indicated the amount of intercalated CuPcTs was 2.3×10^{-4} mol g^{-1}.

3.2 Catalytic Performance of CuPcTs-Zn_2Al-LDH in B-V Oxidation

The catalytic activity of the CuPcTs-Zn_2Al-LDH for the B-V oxidation was examined by performing the oxidation of cyclohexanone to ε-caprolactone in the presence of benzaldehyde at room temperature. Before discussing the catalytic performance of the prepared catalyst, varied solvent including dichloroethane (DCE), dichloromethane (DCM), cyclohexane (CYH) and acetonitrile (ACN), were first optimized. The influence of the solvent on the catalytic activity is mainly related to the polarity, and DCE having the appropriate polarity exhibited the best result (Table 1).

Under the optimized reaction conditions, the conversion of cyclohexanone and selectivity of ε-caprolactone are all near to 100 % after 7 h over CuPcTs-Zn_2Al-LDH. The blank reaction without catalyst showed even low conversion, indicating that the prepared hybrid performed as catalyst in the reaction. CuPcTs-Na_4 and CO_3^{2-}-Zn_2Al-LDH have also been investigated in the B-V oxidation as comparision, and the intercalated sample exhibited the obviously higher catalytic performance. The product yield reached over 99 % when 2.5 equiv. of benzaldehyde was used, indicating that aldehyde efficiency is higher than those in previously reported studies [12, 19, 22].

In addition, the reaction temperature is lower than typical reported work [12–22] including the metalloporphyrin intercalated hydrotalcites [29], where reaction temperatures higher than 40 °C were always employed.

Subsequently, the recyclability of the CuPcTs-Zn_2Al-LDH was examined in the aerobic oxidation of cyclohexanone with shorter reaction time (6 h). The catalyst showed no appreciable reduction of activity even after six runs (Fig. 4), and the selectivities were above 99 %. XRD pattern for the reused catalyst suggested that the layered structure was completely preserved after several reuses (Fig. 1).

Table 1 B-V oxidation cyclohexnaone under different reaction conditions in the presence of benzaldehyde

Entry	Catalyst	Solvent	R[a]	Yield[b] (%)
1	No catalyst	DCE	2.5	34
2	CuPcTs-Na	DCE	2.5	74
3	CO_3^{2-}-Zn_2Al-LDH	DCE	2.5	67
4	CuPcTs-Zn_2Al-LDH	DCE	2.5	>99
5	CuPcTs-Zn_2Al-LDH	DCE	2	92
6[c]	CuPcTs-Zn_2Al-LDH	DCE	3	>99
7	CuPcTs-Zn_2Al-LDH	DCM	2.5	95
8	CuPcTs-Zn_2Al-LDH	CYH	2.5	34
9	CuPcTs-Zn_2Al-LDH	ACN	2.5	16

General conditions: cyclohexanone 2 mmol, catalyst 8.0 mg, reaction time 7 h, room temperature, O_2 10 mL min^{-1}

[a] Equivalent amount of benzaldehyde

[b] The selectivities were all >99 %

[c] Reaction time 6 h

The turnover frequency (TOF) of active site is always used for the precise comparison of the activity of different catalysts. Some characteristic data of other catalytic systems based on O_2/benzaldehyde in the B-V oxidation of cyclohexanone are collected in Table 2. It can be observed that the prepared CuPcTs-Zn_2Al-LDH exhibits higher TOF than most of these catalytic systems. Although FePcS-SiO_2 [12] (Table 2, entry 2) and MnAlPO (Table 2, entry 11) showed higher TOF, but the conversions were low and only moderate yields were obtained. Even doubling the FePcS-SiO_2 catalyst amount, the conversion increased only slightly with the selectivity decreasing below 90 %. The catalytic rate is also lower than our previous reported CoTSPP-Zn_2Al-LDH catalyst (Table 2, entry 8) [29], but the reaction conditions are milder and the efficiency of benzaldehyde increases. Jeong et al. [46] have reported a metalloporphyrins bridged periodic mesoporous organosilicas, and excellent catalytic activity was observed in the B-V oxidation of cyclohexanone.

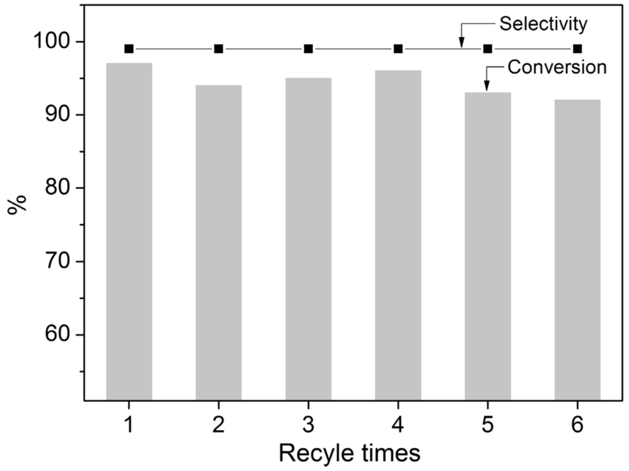


Fig. 4 Reusability of CuPcTs-Zn_2Al-LDH for B-V oxidation. General conditions: cyclohexanone 2 mmol, equivalent amount of benzaldehyde 2.5, catalyst 8.0 mg, reaction time 6 h, room temperature, O_2 10 mL min^{-1}

Table 2 The main results of other catalytic systems based on O_2/benzaldehyde in the B-V oxidation of cyclohexanone

Entry	Catalyst	C[a] (%)	S[b] (%)	TOF (h^{-1})	Ref.
1	CuPcTs-Zn_2Al-LDH	>99	>99	155	This work
2	FePcS-SiO_2	61	100	400	[12]
3	Co_3O_4	98	100	4	[14]
4	InO_x/TUD-1	100	100	9	[16]
5	L-BIOX[c]	>98[d]	>98[d]	33	[17]
6	Ni-Co-HMS-X	100	100	20	[20]
7	CO_3^{2-}-$Mg_3AlFe_{0.3}$-LDH	100	100	36	[24]
8	CoTSPP-Zn_2Al-LDH	>99	>99	298	[29]
9	$[H_4TPP][HPW_{12}O_{40}]$	56.1	43.1	23	[43]
10	Fe-Sn-O mixed oxides	96.6	>99	12	[44]
11	MnAlPO	78	98	257	[45]

[a] Conversion of cyclohexanone

[b] Selectivity of ε-caprolactone

[c] Biogenous iron oxides

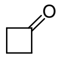
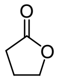
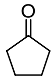
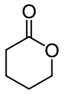
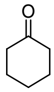
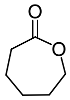
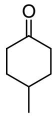
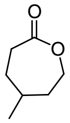
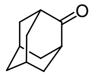
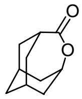
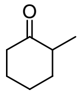
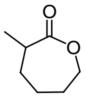
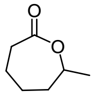
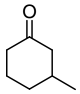
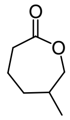
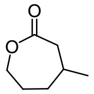
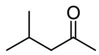
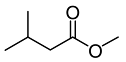
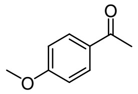
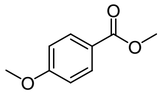
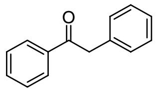
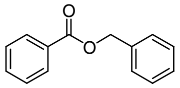
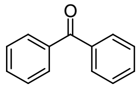
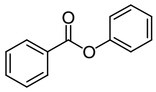
[d] Yield of ε-caprolactone product

However, their catalytic activities for the substrates with increasing bulkiness were even low, and only a 50% conversion was obtained for 2-methylcyclohexanone.

In summary, from the above results and analysis, it is clear that CuPcTs intercalated hydrotalcite is an efficient catalyst for the B-V oxidation through O_2/aldehyde system.

Encouraged by these results, we have carried out CuPcTs-Zn_2Al-LDH catalyzed B-V oxidation of a variety of ketones to better understand both the scope and the generality of the reaction. Table 3 shows the B-V type aerobic oxidation of various ketones in the presence of

Table 3 B-V Oxidation of various ketones over CuPcTs-Zn_2Al-LDH in the presence of benzaldehyde

Entry	Substrate	Product[a]	t (h)	Yield (%)[d]
1[b]			8	92 [50]
2			9	88 [51]
3			7	>99 [52]
4			14	>99 [53]
5			8	97 [54]
6		 (51%)  (49%)	9	>99 [55]
7		 (53%)  (47%)	14	>99 [56]
8			10	Trace
9[c]			16	84 [57]
10[c]			18	65 [58]
11[b]			30	38 [59]

General conditions: substrate 2 mmol, catalyst 8.0 mg, room temperature, 2.5 equiv. of benzaldehyde, O_2 10 mL min^{-1}

[a] Data in brackets are the selectivity of corresponding product

[b] Reaction temperature was 40 °C

[c] Reaction temperature was 30 °C

[d] The characterization of the products can be found in the reference

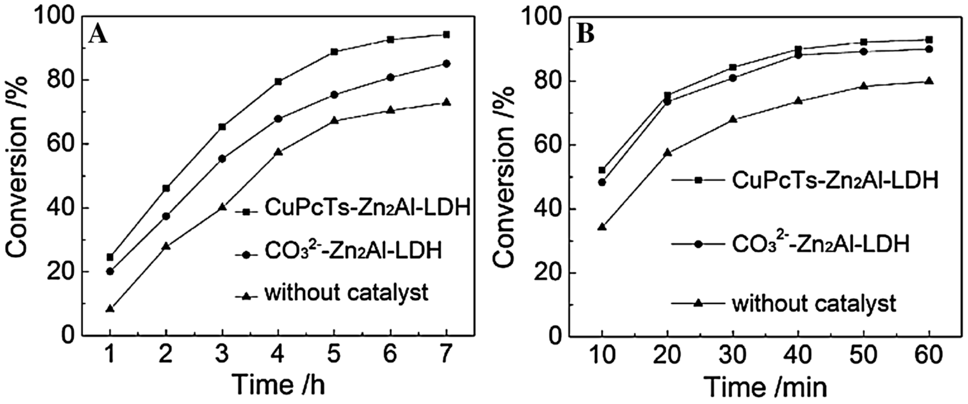
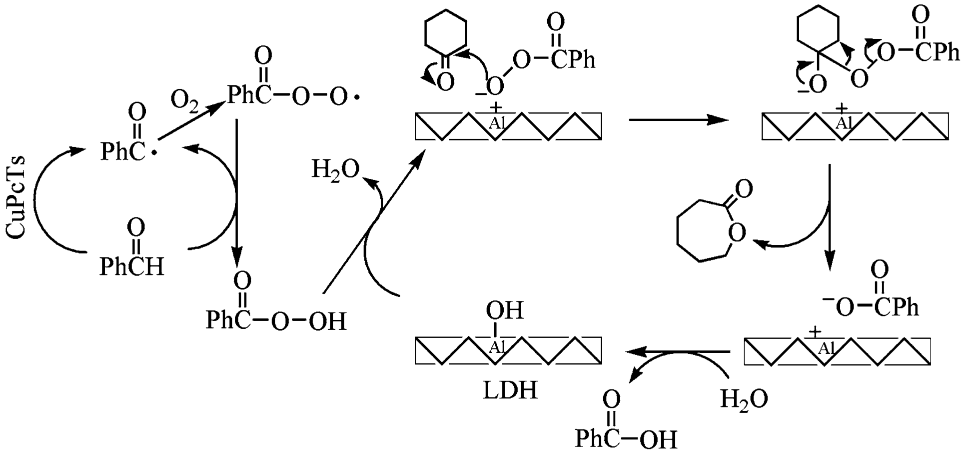


Fig. 5 **a** Oxidation of benzaldehyde to peracid (*m*-chlorobenzaldehyde 2 mmol, O_2 10 mL min^{-1}, catalyst 8.0 mg, room temperature) and **b** Oxidation of cyclohexanone by *m*-chloroperbenzoic acid (substrate 2 mmol, catalyst 8.0 mg, room temperature, 2.5 equiv. of *m*-chloroperbenzoic acid)

Scheme 1 The proposed reaction mechanism of the B-V oxidation catalyzed by CuPcTs-Zn_2Al-LDH



CuPcTs-Zn_2Al-LDH and benzaldehyde. Cyclobutanone, cyclopentanone, cyclohexanone and 4-methylcyclohexanone (Table 3, entries 1–4) were successfully oxidized with high conversion and selectivity. A good yield was also observed when pinacolin was used as substrate (Table 3, entry 5). From asymmetrical ketone like 3-methylcyclohexanone, similar yields of 5-methyl-ε-caprolactone and 3-methyl-ε-caprolactone were obtained (Table 3, entry 6), similar results was also obtained for 2-methylcyclohexanone (Table 3, entry 7), which is different from most of the reported results [13, 29]. However, for the linear ketone like 4-methyl-2-pentanone, the catalytic system is not valid under such conditions (Table 3, entry 8).

Finally, some phenyl containing substrates have been introduced into the reaction system. For the *p*-methoxyacetophenone (Table 3, entry 9), a high 84 % yield was obtained when the temperature increased to 30 °C. Although the yield was a little lower than that reported by Kaneda [47], the reaction temperature was lower and the catalyst amount was reduced with higher selectivity. In addition, the benzyl phenyl ketone and diphenyl ketone (Table 3, entries 10 and 11), which were only investigated in the presence of peroxide [48, 49], could be smoothly transformed under the selected reaction conditions. Interestingly, although no chemoselectivity was observed in the 2-methylcyclohexanone and 3-methylcyclohexanone, only one product formed for the oxidation of benzyl phenyl ketone (which was confirmed by the fact that only benzyl alcohol and benzoic acid were observed in the hydrolyzed products), clearly indicating that CuPcTs-Zn_2Al-LDH could impart chemoselectivity in high degree for these phenyl containing substrates.

Although the reaction rate depends on the chemical structure of ketones, it can be concluded that the prepared CuPcTs-Zn_2Al-LDH catalysts can oxidize various ketones to corresponding lactones or esters under such mild reaction conditions.

To validate our design from the viewpoint of the catalytic mechanism and investigate whether the hybrid CuPcTs-Zn_2Al-LDH can catalyze both steps of B-V oxidation, a series of controlled reactions have been performed. Firstly, CuPcTs-Zn_2Al-LDH was introduced into the first reaction step, namely the oxidation of aldehyde to peracid. For the easy analysis of peracid, *m*-chlorobenzaldehyde instead of benzaldehyde was used and *m*-CPBA was quantified by titration. From the Fig. 5a, it can be observed that the oxidation of benzaldehyde to perbenzoic acid can happen through autoxidation. And both CuPcTs-Zn_2Al-LDH and CO_3^{2-}-Zn_2Al-LDH could accelerate the reaction, whilst CuPcTs-Zn_2Al-LDH exhibited higher activity. On the other hand, the hybrid LDH has also been introduced into the second step using *m*-CPBA as the oxidant, while the blank experiments under the same conditions were performed as comparison. CuPcTs-Zn_2Al-LDH and CO_3^{2-}-Zn_2Al-LDH showed comparable activity in the reaction (Fig. 5b), because the catalytic performance of hydrotalcites for this step is mainly related to their basicity [22]. It is obviously concluded that CuPcTs-Zn_2Al-LDH could accelerate both of the reactions and act as the bifunctional catalyst for the B-V oxidation under the selected conditions.

On the basis of the above results and analysis, we suppose that, in the CuPcTs-Zn_2Al-LDH catalyzed B-V oxidation of ketones by the O_2/aldehyde system, the hybrid not only catalyzed the oxidation of aldehyde to form the peroxyacid, but also accelerated the reaction of ketone with peroxyacid to corresponding product. A possible mechanism was proposed in Scheme 1 based on our observations and reported results [22, 60, 61]. Perbenzoic acid is firstly formed with oxygen under the catalysis of copper phthalocyanine. Then the reaction of the peroxyacid with OH group on the hydrotalcite surface gives a metal perbenzoate species and H_2O. Then, the perbenzoate species attacks ketone to form a metal alkoxide intermediate, which further converts into lactone accompanied with the formation of benzoic acid anion. After reacting with H_2O, benzoic acid is produced and Zn Al hydrotalcite having OH groups is recovered.

4 Conclusion

A bifunctional catalyst has been designed and prepared by intercalation of CuPcTs into ZnAl hydrotalcite on the basis of the reaction mechanism of B-V oxidation. Varied characterizations of the sample indicated that CuPcTs has been successfully introduced into the interlayer of ZnAl hydrotalcite. The material could smoothly catalyze the B-V type oxidation from ketones to corresponding lactones or esters in the presence of benzaldehyde, and tolerated a wide range of substrates. The catalyst recycling tests suggest that the durability of the CuPcTs-Zn_2Al-LDH is quite good in the tested reaction conditions. The controlled experiments have revealed that the prepared hybrid could catalyze both the oxidation of benzaldehyde to peroxyacid and the formation of lactones or esters, indicating its bifunctional role in B-V oxidations. The protocol would be helpful in the rational design of environmentally friendly and efficient catalytic systems.

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