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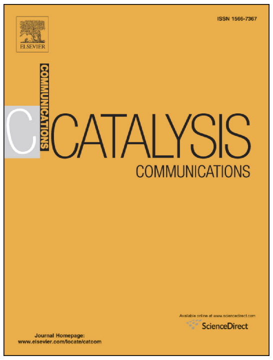

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Efficient aerobic oxidation of ethylbenzene accelerated by Cu species in hydrotalcite

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Abstract: The simply prepared CuMgAl hydrotalcite (CuMgAl-LDH) has been developed as an efficient catalyst for the aerobic oxidation of ethylbenzene to acetophenone in the presence of N-Hydroxyphthalimide (NHPI). Various alkyl arenes could be tolerated under the selected reaction conditions. The kinetic study showed that the oxidation of ethylbenzene is a first-order reaction over CuMgAl-LDH. The mechanism study indicated that CuMgAl-LDH could accelerate not only the conversion of ethylbenzene, but also the transformation of the alcohol intermediate to ketone. The positive effect of surface basicity of the catalyst on the reaction has been observed in the aerobic oxidation of the ethylbenzene.

Keywords: CuMgAl hydrotalcite, aerobic oxidation, ethylbenzene, bifunctional catalysis, Hammett experiment

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Introduction

The selective oxidation of alkylbenzenes to the corresponding ketones has been studied over the past decades, as the products are important intermediates in the field of fine chemicals [1, 2]. Transition mental oxides, such as oxides of manganese and chromium had been used for the transformation, but a large amount of hazardous wastes and by-products were produced, creating issues of handling and disposal [3]. Tert-butyl hydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) are also commonly used as oxidants for the oxidation, however, peroxides are corrosive and unstable at room temperature, which make them less suitable for large scale industrial reactions [4, 5]. Dioxygen is an economically and environmentally feasible oxidants for the large-scale processing [6, 7]. However, it is difficult for dioxygen to directly oxidize the strong bond of C–H for its inertness [2]. Although some catalysts based on metal complexes or oxides have been developed for the oxidation of alkyl aromatics using molecular oxygen as the sole oxidant, but the catalytic performances are still not satisfactory [1, 8-13].

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The introduction of NHPI as an initiator for the selective oxidation of hydrocarbons can enable the reaction to proceed under mild conditions and improve the yield of the products, which has attracted wide attention in recent years, and various catalytic systems have been investigated [14-19]. The metal-free *g*-C_3N_4 / NHPI system has been used for the selective aerobic oxidation of ethylbenzene by visible light induction under mild conditions, but it could only give a 27% conversion of ethylbenzene in 23 h [16]. Schmieder et al. [17] reported a novel MOF (CFA-8) that could catalyze the oxidation of alkylbenzene with NHPI under mild conditions. However, the conversion of ethylbenzene was only 60% with a quite long reaction time of 70 h. Rajabi's group [20] investigated the aerobic oxidation of alkylbenzene using a silica supported cobalt (II) Salen complex/NHPI, but the yield of ethylbenzene was only 78%. Habibi et al. [21] developed a SiO_2/Al_2O_3 immobilized manganese catalyst, which could provide a high 95% conversion of ethylbenzene with a 99% selectivity of acetophenone. Metallophthalocyanine (M=Co, Cu, Mn and Fe) intercalated layered double hydroxides have been prepared and investigated in the aerobic oxidation of alkyl aromatics [22]. Although the hybrid catalyst exhibited efficient catalytic performance, its preparation method was quite complicated, significantly limiting its wide application. Copper-containing heterogeneous catalysts have been extensively studied in the aerobic oxidation of alkylarenes, including copper phosphate [23], Cu@PILC (poly ionic liquid complexes) [24], Cu–$CuFe_2O_4$@HKUST-1 (metal–organic frameworks) [4], and etc. However, most of the catalytic systems suffered from the low efficiency, complicated preparation process, harsh reaction conditions, or high-cost of catalysts. Developing efficient catalysts based on commercially available materials for the oxidation of alkyl arenes is still highly desirable.

In the aerobic oxidation of ethylbenzene, some researchers have found that introduction of base into the reaction system could improve the catalytic activity [25]. On the other hand, layered double hydroxide (LDH) is a typical basic material with hydrotalcite structure, which could be conveniently prepared by coprecipitation method. Therefore, on the basis of the above results, CuMgAl hydrotalcite (CuMgAl-LDH) has been prepared and investigated in the aerobic oxidation of alkylarenes in the present study. Excellent catalytic performance has been observed in the aerobic oxidation ethylbenzene in the presence of NHPI.

Experimental

Preparation and characterization of LDH catalyst

CuMgAl-LDH was prepared by coprecipitation method according to the report [26] (see the supporting information for the detailed preparation process). And the prepared catalyst was characterized by x-ray diffraction pattern (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectra, Thermogravimetric analysis (TG) and inductively coupled plasma analysis (ICP), the surface area was calculated using the BET method and the pore size distributions

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were deduced through the BJH method. (see the supporting information for the detailed description of instruments used for the characterization).

General catalytic procedure for the aerobic oxidation

In a typical procedure, the oxidation was carried out in a carousel parallel reaction tube under molecular oxygen. A suspension of catalyst (25 mg), NHPI (0.1 mmol), chlorobenzene (inert internal standard, 0.3 mmol), ethylbenzene (1 mmol), and benzonitrile (2 mL), were magnetically stirring at 100 ºC under oxygen atmosphere. Qualitative analysis of all the products was performed on GC-MS (Shimadzu GCMS-QP2010) with a DB-5 chromatographic column, and quantitative analysis was finished on GC-FID (Shimadzu GC-2010AF) with a SE-30 chromatographic column using chlorobenzene as the internal standard.

Results and discussion

Characterization of CuMgAl-LDH

The XRD pattern of the CuMgAl-LDH depicted in Fig. 1 shows the typical well-crystallized diffraction pattern of a hydrotalcite-like phase [27, 28]. The sharp reflections around $2\theta = 11.3$, 22.6 and 33.9° are related to (003), (006) and (009), respectively; broad peak for (015) located at about 40° [29, 30]. Further, the lattice parameters “c” corresponding to the sum of the thickness of a brucite-like layer and an interlayer can be calculated from (003) reflection. A value of 7.89 Å was obtained for CuMgAl-LDH sample, indicating the main interlayer anions were carbonate ions [31]. As shown in Fig. S1A for the infrared spectrum of CuMgAl-LDH, it can be found that the sample shows a wide and strong band at about 3456 cm^{-1} due to the -OH stretching vibration of the interlayer hydroxyl group and water molecules. The absorption peak at 1637 cm^{-1} is the bending vibration of water molecules inside the hydrotalcite, and the strong stretching vibration at 1384 cm^{-1} is the carbonate anion between the interlayers. In the 400-1000 cm^{-1} area, it is due to the vibration of cation-oxygen bond in hydrotalcite. The SEM image of CuMgAl-LDH obviously shows the plate-like agglomerated crystals, also demonstrating the formation of hydrotalcite structure (Fig. S1B). TG/DTG curve of CuMgAl-LDH is depicted in Fig. S1C. The peak at 170.0 ℃ corresponds to the loss of water on the surface and interlayer water of hydrotalcite, while 593.1 ℃ can be attributed to the dehydration of hydroxyl groups on the hydrotalcite layer and the loss of CO_2 in the intermediate layer. The data of ICP analysis in Table S1 shows that the ratio of Cu/Mg/Al was almost identical to the theoretical value.

Fig. 1

Catalytic performance of CuMgAl-LDH in the aerobic oxidation of ethylbenzene with NHPI

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In this present study, CuMgAl-LDH was selected as the catalyst in the aerobic oxidation of ethylbenzene (Table S2), and the reaction conditions were firstly optimized. Acetophenone (AcPO) was the main product and 1-phenylethanol (PEA) was the by-product. The effect of the solvent was first investigated in the oxidation of ethylbenzene. A relatively higher conversion of 99.3% and a selectivity of 97.7% (Table 1, entry 1) were achieved when benzonitrile was used as the solvent, which might be due to its appropriate polarity [32]. When NHPI was used in aerobic oxidation, polar solvents, such as acetonitrile, were usually used as solvents, however, acetonitrile gave rather low conversion of 45.4% owing to its low boiling point (entry 3). With increase of temperature, the selectivity of PEA declined, the conversion of ethylbenzene and the selectivity of AcPO increased (entry 8~11). When temperature increased to 120 ℃, the conversion changed slightly. The production of benzoic acid was favorable under higher temperatures, which should be related to the over-oxidation. The conversion of ethylbenzene increased with the increase of the amount of CuMgAl-LDH (entry 13, 14). And the appropriate catalyst loading for oxygenation should be about 25 mg and ethylbenzene could be completely converted after 5 h (entry 19). The stability and recyclability of CuMgAl-LDH in the aerobic oxidation have been investigated and the results indicated that the catalyst was catalytically and structurally stable under the selected reaction conditions (Figure S2). Some characteristic data for the catalytic aerobic oxidation of ethylbenzene to acetophenone based on copper-containing catalytic systems were listed in Table S3, suggesting that CuMgAl-LDH is a high-effective catalyst among the mentioned copper-containing catalysts.

Table 2

Kinetic study has also been conducted in the present research. After excluding the effects of internal and external diffusion (Fig. S3), the experiments were investigated under different temperatures to study the kinetic aspects of the aerobic oxidation of ethylbenzene. The fitting results indicated that the oxidation is a first order reaction, and “C” represented the molar concentration of the substrate (Fig. 2A).

The k value can be obtained by the Arrhenius equation, and the parameters of the Arrhenius equation (Equation 1) can be deduced from the plot of ln |k| to 1/T.

$$ln\,|k| = lnA_0 - \frac{E_a}{RT}$$

“E_a” represents activation energy (kJ/mol), “A_0” is the pre-exponential factor (min^{-1}), “R” represents molar gas constant with a value of 8.314 J/(mol·K).

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A multiple regression analysis with this expression of the constants against temperature was depicted in Fig. 2B. The slope and the intercept of the equation can be obtained as -4234.5980 and 9.4373, respectively. The value of the apparent activation energy (E_a) and the pre-exponential factor (A_0) of CuMgAl-LDH can be calculated through equation 1, and they are 35.2 kJ/mol and 1.2×10^4 min^{-1}, respectively.

To further elucidate the catalytic performance of CuMgAl-LDH, CuMgAl hydroxide was investigated in the reaction for comparison, which was prepared via directly coprecipitated by NaOH and $Cu(NO_3)_2\cdot6H_2O$. Kinetic study of CuMgAl hydroxide was also investigated by the same method, and the value of E_a and A_0 were 52.3 kJ/mol and 2.4×10^6 min^{-1} (Fig. S4). The apparent activation energy in the case of CuMgAl-LDH was quite lower than that of CuMgAl hydroxide, indicating the higher catalytic activity of CuMgAl-LDH, which should be related to its unique structure.

Fig. 2.

Discussion of the possible reaction pathways

First, the CuMgAl-LDH-catalyzed system was investigated in the aerobic oxidation of other alkyl aromatic hydrocarbons (Table 2). *p*-methoxyethylbenzene could be completely converted within 3 h, while the conversions of *p*-bromoethylbenzene and *p*-nitroethylbenzene were lower, indicating that the electron-donating substituents at the *para*- site can accelerate oxidation. On the other hand, the conversion of some substrates including 4-ethylbiphenyl (entry 4), propylbenzene (entry 5) and fluorene (entry 6), decreased under the selected reaction conditions, which might be due to the effect of steric hindrance. The conversion of tetralin reached 74% with a 84% selectivity of tetralone (entry 7). And diphenylmethane could give a 97% conversion with a high 91.5% selectivity of benzophenone when increasing the temperature to 120 ℃ (entry 8). When ethyl phenol was used as substrates, almost no reaction could be observed, which might be attributed to the free radical path of the reaction. Toluene was oxidized slowly in this system with a 16% conversion, but an excellent selectivity of benzaldehyde (entry 10) could be obtained. In general, the present catalytic system could efficiently catalyze the selective aerobic oxidation of various alkyl aromatic hydrocarbons under selected conditions.

Table 2.

In order to reveal the relation between the catalytic performance and structure of CuMgAl-LDH, a range of controlled experiments were performed. (Table 3). The reaction in the absence of catalyst gave a 13.6% conversion for ethylbenzene and a 81% selectivity for acetophenone, implying that CuMgAl-LDH could accelerate the conversion of ethylbenzene as well as increase the selectivity of acetophenone (entry 4). Without NHPI, the substrate could not be converted (entry 3), suggesting that NHPI was essential in this catalytic system. It is well known that NHPI is a free radical oxidation catalyst. NHPI does not accelerate the decomposition of hydroperoxide like transition metals. The

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catalytic activity of NHPI results from phthalimide-Noxyl radical (PINO) generation in the propagation step of the oxidation process. In addition, when air was used instead of pure O_2, the reactivity was significantly reduced (entry 6), and the reaction does not occur under N_2 conditions (entry 5). The above results implied that the concentration of O_2 played an important role in the conversion of ethylbenzene and the selectivity of acetophenone in the present system. When using copper chloride as the catalyst, the conversion rate was 53% and the selectivity was 84% (entry 8), while MgAl-LDH almost did not promote the reaction (entry 9). These results indicated that copper species was the activity species.

When CuMgAl hydroxide was introduced to the reaction (entry 5), the conversion of ethylbenzene decreased to 79% and the selectivity of acetophenone decreased to 82%, which were consistent with the kinetic data. The BET surface area of the CuMgAl-LDH was 73.2 m^2/g, significantly higher than that of CuMgAl hydroxide (Table S1), which might be responsible for the difference of the activity to some extent. The Hammett indicator method was used to analyze the basic sites of the catalysts instead of CO_2-TPD analysis (temperature-programmed desorption of carbon dioxide), because LDH samples required high-temperature pretreatment in CO_2-TPD analysis, which is bound to destroy the structure of the LDH samples. The data in Table S4 showed that the basicity of CuMgAl-LDH was higher than CuMgAl hydroxide. To test the effect of basicity on the catalytic performance in the aerobic oxidation of the ethylbenzene, 10 mg Na_2CO_3 was introduced to the oxidation when copper chloride was used as the catalyst (Table 3, entry 10). Both the conversion of ethylbenzene and the selectivity of acetophenone increased to some extent, suggesting that surface basicity of hydrotalcites has advantages in the selective oxidation of aromatic hydrocarbons.

In addition, the reaction was quenched when one equivalent of 2,6-di-tert-butyl-4-methylphenol (BHT) was added (entry 2), indicating that free radicals formed as important intermediates for the reaction [14, 15]. Phthalimido-*N*-oxyl radical (PINO) formed in the propagation step of the oxidation process in the presence of NHPI, hydroperoxide formed subsequently through radical reactions [33], which has been widely recognized.

Table 3.

Alcohol was observed in the cases of $CuCl_2$ and CuMgAl hydroxide, but not found in CuMgAl-LDH. It is speculated that alcohol is more easily oxidized to ketone under the catalysis of CuMgAl-LDH, which might be the possible reason for the high selectivity. To examine the speculation, the mixture of ethylbenzene and phenethyl alcohol were introduced as the reactants under the selected conditions. The result in Fig. S5 obviously indicated that the oxidation rate of phenethyl alcohol was evidently higher than that of the oxidation of ethylbenzene, suggesting that CuMgAl-LDH could accelerate the transformation of the alcohol intermediate to ketone. On the other hand, the

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negative slope of the Hammett plot (ρ≈-0.79) (Fig. S6) demonstrated that electron-demanding transition state involved in the oxidation, indicating the more electron-rich substrates with higher oxidation rates [34].

Based on the obtained results and some literatures [4, 23, 24, 33, 35], a possible reaction path (Scheme 1) is proposed. Firstly, NHPI was abstracted a hydrogen to generate PINO under the catalysis of the CuMgAl-LDH. PINO could abstract an active hydrogen atom from ethylbenzene to generate NHPI. The generated ethylbenzene radical was trapped by molecular oxygen to generate ethylbenzene peroxy radical, which further converted to PEHP in the presence of NHPI. PEHP decomposed to acetophenone and 1-phenylethanol subsequently. In the present CuMgAl-LDH/NHPI/O_2 system, 1-phenylethanol could be further oxidized to acetophenone through a radical process [4].

Scheme 1.

Conclusions

Developing efficient catalysts based on non-noble metals for the aerobic oxidation of ethylbenzene in the presence of NHPI is highly desirable. In the present work, CuMgAl-LDH has been found to be an efficient catalyst for the selective oxidation of alkylbenzene. A wide variety of substrates were well tolerated in the present protocol. The kinetic study showed that the oxidation of ethylbenzene is a first-order reaction over CuMgAl-LDH with the activation energy (E_a) and pre-exponential factor (A_0) being 35.2 kJ/mol and 1.2×10^4 min^{-1}. The controlled experiments showed that the basicity of CuMgAl-LDH has a great influence on the catalytic activity. The corresponding alcohol was thought to be formed as an intermediate product, which could be rapidly oxidized to ketone under the catalytic system. The possible reaction pathway for the oxidation of ethylbenzene has been proposed based on obtained results, series of controlled experiments and Hammett experiment.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Tables and Figures

Fig. 1. XRD pattern of CuMgAl-LDH

Table 1 The effects of solvent, reaction temperature, amount of catalyst and reaction time in the oxidation of ethylbenzene.

Fig. 2. First order kinetics fit of aerobic oxidation of ethylbenzene under different temperatures (A), Arrhenius plot for the aerobic oxidation of ethylbenzene over CuMgAl-LDH (B).

Table 2. Catalytic aerobic oxidation of varied substrates under CuMgAl-LDH

Table 3. The catalytic results of controlled experiments.

Scheme 1. The proposed mechanism of the oxidation of ethylbenzene by CuMgAl-LDH in the presence O_2/NHPI

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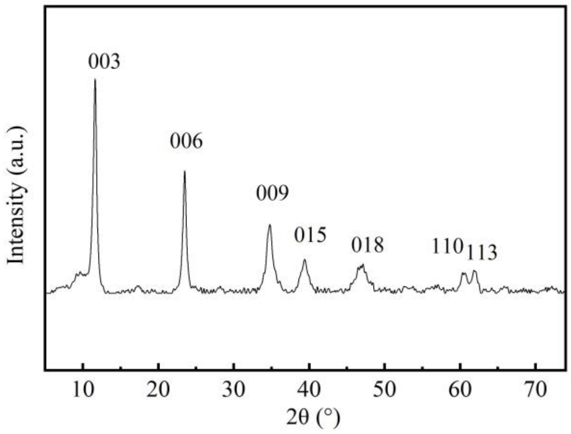

Fig. 1. XRD pattern of CuMgAl-LDH

Table 1 The effects of solvent, reaction temperature, amount of catalyst and reaction time in the oxidation of ethylbenzene.

Entry	Solvent	Temperature (℃)	Catalyst amount (mg)	t (h)	Conv. (%)	Sel. (%)	
						AcPO	PEA
1	benzonitrile	100	50	5	99.3	97.7	trace
2	DMF	100	50	5	1.9	88.4	11.3
3	acetonitrile	100	50	5	45.5	77.4	22.6
4	*p*-xylene	100	50	5	5.3	83.2	16.8
5	1,2-Dichloroethane	100	50	5	2.1	78.0	22.0
6	1,4-Dioxane	100	50	5	6.1	86.5	17.5
7	H_2O	100	50	5	trace	-	-
8	benzonitrile	60	50	3	58.1	78.1	21.9
9	benzonitrile	80	50	3	82.3	86.4	13.6
10	benzonitrile	100	50	3	92.1	98.1	1.9
11	benzonitrile	120	50	3	93.3	95.6	4.4
12	benzonitrile	100	0	3	13.1	96.2	3.8
13	benzonitrile	100	15	3	77.0	97.6	2.4
14	benzonitrile	100	25	3	91.9	99.3	0.7
15	benzonitrile	100	50	3	93.0	99.4	0.6
16	benzonitrile	100	25	1	54.4	97.6	2.4
17	benzonitrile	100	25	2	80.0	98.9	1.1
16	benzonitrile	100	25	4	96.6	99.4	0.6
19	benzonitrile	100	25	5	99.1	99.2	0.8

Reaction conditions: CuMgAl-LDH, ethylbenzene 1 mmol, NHPI 0.1 mmol, solvent 2 mL, O_2 atmosphere.

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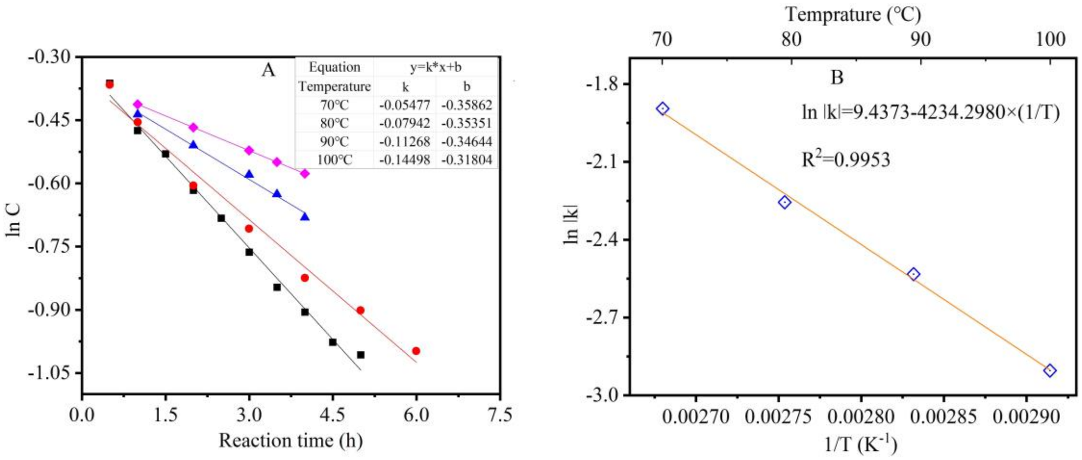

Equation	y=k*x+b	
Temperature	k	b
70°C	-0.05477	-0.35862
80°C	-0.07942	-0.35351
90°C	-0.11268	-0.34644
100°C	-0.14498	-0.31804

Reaction conditions: ethylbenzene 2 mmol, CuMgAl-LDH 25 mg, benzonitrile 3 mL, O_2 atmosphere (A).

Fig. 2 First order kinetics fit of aerobic oxidation of ethylbenzene under different temperatures (A), Arrhenius plot for the aerobic oxidation of ethylbenzene over CuMgAl-LDH (B).

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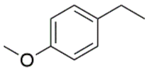
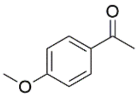
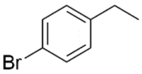
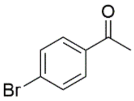
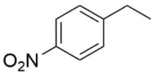
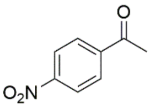
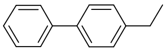
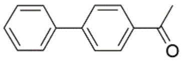
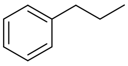
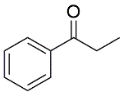
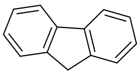
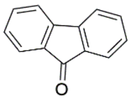
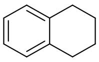
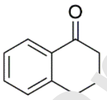
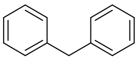
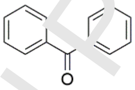
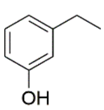
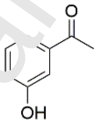
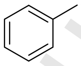
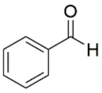
Table 2. Catalytic aerobic oxidation of varied substrates under CuMgAl-LDH

Entry	Substrate	Product	Conv. (%)	Sel. (%)
1[a]			99	99
2			64	99
3			24	95.7
4			73	99
5			56	99
6			96.6	99
7			73.7	83.7
8[b]			97	91.5
9			-	-
10			16	99

Reaction conditions: substrate 1 mmol, NHPI 0.1 mmol, CuMgAl-LDH 30 mg, benzonitrile 2 mL, 5 h, 100 °C, O_2 atmosphere.

[a] 4h, [b] 120 °C

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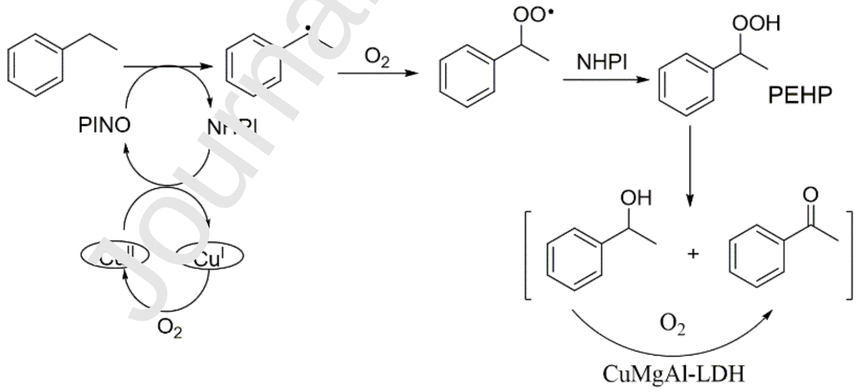
Table 3. The catalytic results of controlled experiments.

Entry	Catalyst	oxidant	Add.	Conv. (%)	Sel. (%)	
					AcPO	PEA
1	CuMgAl-LDH	O_2	NHPI	99	99	trace
2[a]	CuMgAl-LDH	O_2	NHPI	0	-	-
3	CuMgAl-LDH	O_2	-	trace	-	-
4	-	O_2	NHPI	13.6	81	19
5	CuMgAl-LDH	N_2	NHPI	0	-	-
6	CuMgAl-LDH	Air	NHPI	62	64	36
7	CuMgAl hydroxide	O_2	NHPI	79	82	18
8	$CuCl_2$	O_2	NHPI	53.3	84	16
9	MgAl-LDHs	O_2	NHPI	13.7	89	11
10[b]	$CuCl_2$	O_2	NHPI	64.3	89	11

Reaction conditions: ethylbenzene 1 mmol, NHPI 0.1 mmol, CuMgAl-LDH 25 mg, benzonitrile 2 mL, 5 h.

[a] 1 mmol of BHT was introduced.

[b] 10 mg Na_2CO_3 was introduced.



Scheme 1 The proposed mechanism of the oxidation of ethylbenzene by CuMgAl-LDH in the presence O_2/NHPI

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CRediT author statement

Xuan Dai: Conceptualization, Methodology, Formal analysis, Investigation, Writing-Original Draft, Writing-Review & Editing and Visualization

Jiaming Guo: Software, Validation and Data Curation

Shuangling Tang: Supervision and Project administration

Xinhua Peng: Writing-Review & Editing,

Xuegen Zheng: Validation and Resources

Ou Jiang: Validation and Resources

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No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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1 CuMgAl-LDH can efficiently catalyze the aerobic oxidation of ethylbenzene in the presence of NHPI.

2 Various substrates can be tolerated under the CuMgAl-LDH/NHPI/O_2 system.

3 The kinetic study showed that the oxidation of ethylbenzene is a first-order reaction over CuMgAl-LDH.

4 The mechanism for the oxidation over CuMgAl-LDH with NHPI was systematically studied.

5 The positive effect of surface basicity of the catalyst on the reaction has been observed.

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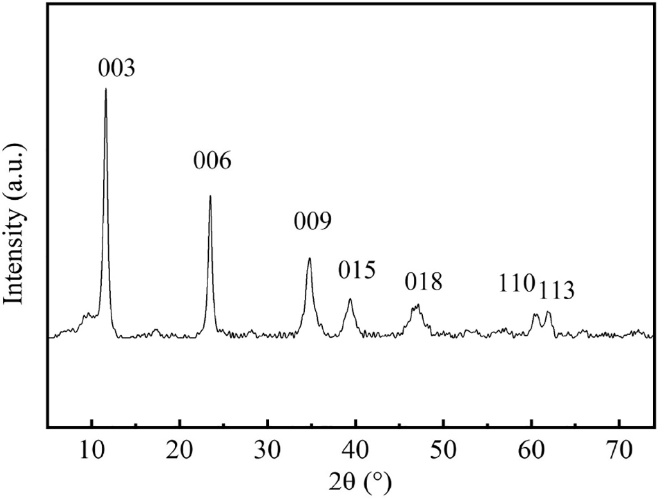
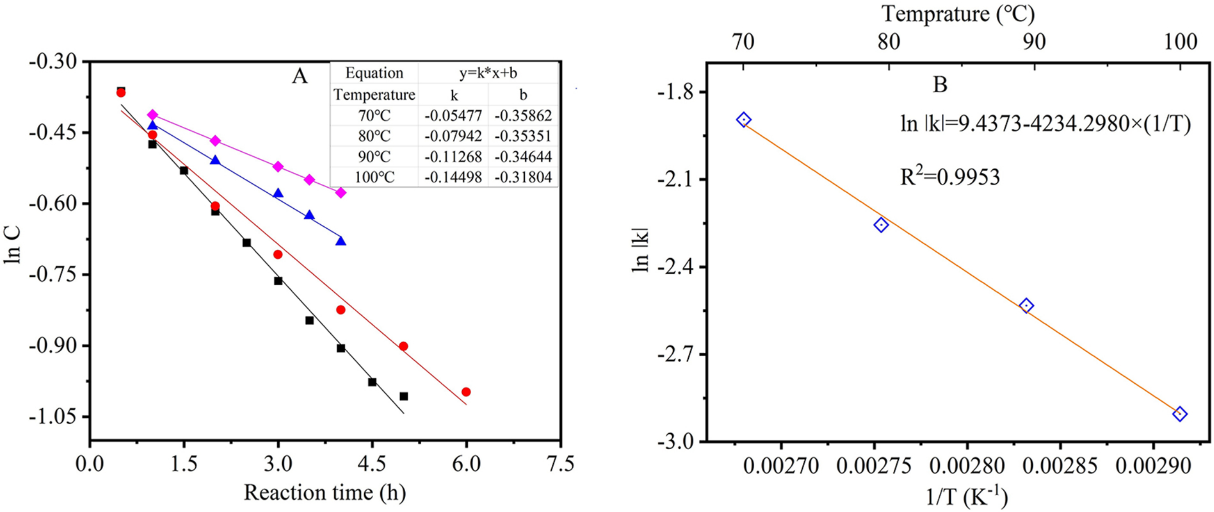


Figure 1



Equation	y=k*x+b	
Temperature	k	b
70°C	-0.05477	-0.35862
80°C	-0.07942	-0.35351
90°C	-0.11268	-0.34644
100°C	-0.14498	-0.31804

Figure 2