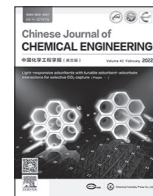




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Full Length Article

Solvent-free partial oxidation of cyclohexane to KA oil over hydrotalcite-derived Cu-MgAlO mixed metal oxides



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ABSTRACT

A highly efficient and stable hydrotalcite-derived Cu-MgAlO catalyst was developed for the partial oxidation of cyclohexane with molecular oxygen. The physical–chemical properties of Cu-MgAlO catalysts were studied, and the results indicated that the copper component had been successfully introduced into the hydrotalcite unit layer structure. The catalytic reaction results showed that copper as the active species could activate C–H bond and effectively promote the decomposition of cyclohexyl hydroperoxide (CHHP) to the mixture of cyclohexanol and cyclohexanone (KA oil). 8.3% of cyclohexane conversion and 82.9% of selectivity for KA oil were obtained over 9%Cu-MgAlO catalyst at 150 °C with 0.6 MPa of oxygen pressure for 2 h. Especially, its catalytic performance was still stable after five runs.

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1. Introduction

Partial oxidation of saturated hydrocarbons to valuable products is an important organic reaction. Typically, the mixture of cyclohexanol and cyclohexanone (KA oil) from the aerobic oxidation of cyclohexane are used as the irreplaceable intermediates for production of nylon-6 and nylon-66 [1–3]. The present industrial process for the oxidation of cyclohexane with air was performed in the presence of homogeneous cobalt salts or no catalyst, which controls the cyclohexane conversion at 3%–5% to achieve higher KA oil selectivity (82%–84%) [4]. Therefore, it is urgent to develop a more simple and efficient catalyst to improve the efficiency of this process.

Some heterogeneous catalysts have been explored in cyclohexane oxidation because of their easy separation and recycling. These catalysts include metal complexes ([Fe^{II}(L)OTf₂] [5], CoTPSC [6], transition metal oxides (MnCeO_x [7], Ti-Zr-Co [8], Mn₂Co₂O_x [9]), molecular sieves (Co-SAPO-5 [10], Co/SBA-15 [11]), M-TUD-1 [12]), nano-catalysts [13,14], photo-catalysts (MnBR₈PI [15]), Pt/TiO₂ [16], BiVO₄ [17]) etc. Copper as an abundant and inexpensive

transition metal has been widely used in organic catalytic reactions [18,19]. Pombeiro *et al.* [20,21] used copper-containing coordination polymers as an efficient catalysts for peroxidative oxidation of cyclohexane to KA oil by H₂O₂ in acetonitrile. Liu *et al.* [22] prepared an amorphous copper-chromium oxides catalyst by a sol–gel method and used it in the selective oxidation of cyclohexane using H₂O₂ as oxygen source. However, copper oxides directly used as catalysts are easy to be deactivated mainly due to particle agglomeration or metal sintering [23]. Hence, many researchers attempted to immobilize copper oxides on different supports to improve catalytic activity and stability. For example, Pérez *et al.* [24] prepared immobilized the copper complexes on SBA-15 as a stable catalyst for selective oxidation of benzyl alcohol to benzaldehyde. Notestein *et al.* [25] reported that the copper oxides well dispersed on meso-structured KIT-6 silica can effectively catalyze the oxidative dehydrogenation of cyclohexane to benzene. Hydrotalcite or hydrotalcite-derived compounds as catalysts have received increasing attention because of their reconfigurable properties, high thermal stability and homogeneous dispersion of metal cations [26–30]. It is serving as a support for the preparation of different mixed metal oxides to catalytic in oxidation and dehydrogenation reaction, such as partial oxidation of methane over Ni/MgAlO [31], oxidative dehydrogenation of propane over

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Co-MgAlO [32], and catalytic dehydrogenation of cyclohexane over Pt/MgAl(Sn)O [33]. Excitedly, these catalysts show excellent catalytic performance.

Herein, we prepared the hydrotalcite-derived Cu-MgAlO mixed metal oxides catalysts for the partial oxidation of cyclohexane toward KA oil employing O_2 as oxidant without any solvent. The physical–chemical properties of catalysts were investigated by XRD, XPS, SEM, UV–vis, FT-IR, H_2 -TPR, ICP-AES and BET characterization. Moreover, the catalytic performance and stability of Cu-MgAlO catalysts were evaluated, and the reaction conditions were also optimized.

2. Experimental

2.1. Synthesis of the catalysts

The hydrotalcite-derived of Cu-MgAlO mixed metal oxides were synthesized by co-precipitation [34,35]. Typically, 12.80 g of Mg(NO_3) $_2$ ·6H $_2$ O, 10.42 g of Al(NO_3) $_3$ ·9H $_2$ O and 1.34 g of Cu(NO_3) $_2$ ·3H $_2$ O were gradually dissolved into 300 ml distilled water at 60 °C. Then the mixture solution of Na $_2$ CO $_3$ and NaOH was added at the rate of one drop per second until the pH value was regulated to 9–10. The generated suspension was aging to form a hydrotalcite phase at 60 °C for 12 h. Finally, the precipitates were washed constantly using distilled water until the filtrate was neutral. The obtained slurry was dried at 100 °C for 12 h, which marked as the 9%Cu-MgAl-LDH. The obtained 9%Cu-MgAl-LDH was calcined at 600 °C for 6 h, and the resulting mixed metal oxides were marked as 9%Cu-MgAlO catalysts. According the different addition amount of copper, 2% (mass) Cu-MgAlO, 4%Cu-MgAlO, 9%Cu-MgAlO and 18%Cu-MgAlO catalysts were respectively obtained.

2.2. Characterization of catalysts

BET data of samples were collected on a Quantachrome Instruments NOVA-2200e using N_2 adsorption at 77 K. The XRD patterns of the samples were obtained on a Japan Rigaku D-Max-2550 V $^+$ diffractometer using CuK $_{\alpha}$ radiation. The XPS technique (K-Alpha 1063) was used to exam the chemical states of copper element, and C1s (binding energy 284.6 eV) signal was used as the reference. SEM images of the samples were collected on a JSM-6610LV with the accelerating voltage of 220 kV. The UV–vis DRS spectra were recorded on a UV-2550 spectrometer with an barium sulfate as reference. The FT-IR spectroscopy was operated on a Nicolet 380 spectrometer with a potassium bromide disk. H_2 -TPR was performed on an Quantachrome Instruments CHEMBET 3000. Elemental analyses were carried out on an Agilent ICP-OES730 instrument.

2.3. Catalytic property tests

The cyclohexane oxidation reaction was tested in a 250 ml autoclave reactor. Typically, 60 g of cyclohexane and 0.05 g of catalyst were added into the reactor. The reactor was heated to 150 °C after sealing, then oxygen was injected and maintained the pressure of 0.6 MPa. After reaction for 2 hours, the reactor was cooled to 10 °C in a ice bath. The liquid mixture was dissolved with ethanol and then separated by centrifugation. The solid catalyst was washed several times by ethanol and dried in a vacuum at 80 °C for 6 h. The products of cyclohexanone (K) and cyclohexanol (A) were analyzed by a gas chromatography (Shimadzu GC-2010 PLUS) equipped with a FID detector and a capillary column (RTX-5, column length: 30 m; internal diameter: 0.32 mm). The injection port temperature and the detector temperature were 250 °C and 260 °C, respectively. The initial temperature was maintained at 100 °C for

1.5 min, then raised 20 °C·min $^{-1}$ to 220 °C and held at this temperature for 3 min. Nitrogen was used as the carrier gas and chlorobenzene was selected as the internal standard. The acid and ester were determined by acid-base titration, and the cyclohexyl hydroperoxide (CHHP) was quantitative analyzed by iodometric titration.

3. Results and Discussion

3.1. Characterization of catalysts

The XRD patterns of 9%Cu-MgAl-LDH, MgAlO, fresh and used 9%Cu-MgAlO samples were displayed in Fig. 1. Clearly, the diffraction peaks of synthesized Cu-MgAl-LDH presented an typical hydrotalcite structure (JCPDS 89-0460, standard card of MgAl-LDH), indicated that copper element had been successfully introduced into the hydrotalcite unit layer structure [36,37]. After calcination to become Cu-MgAlO sample, the diffraction peaks of hydrotalcite structure were disappeared, and new peaks at 2θ of 36.1°, 43.3° and 62.8° considered as periclase MgO phase were occurred. It should be noted that the characteristic diffraction peaks of copper species had not been observed in Cu-MgAlO sample, this might be due to copper species were inserted into layer structure or highly dispersed on the composites. These results were agreement with that of the literatures reported [1,38]. In addition, the characteristic diffraction peaks of used 9%Cu-MgAlO were almost the same as that of fresh 9%Cu-MgAlO sample, which indicated that the Cu-MgAlO catalyst was very stable in the cyclohexane oxidation reaction.

In order to obtain the textural properties and morphology of catalysts, the BET, ICP-AES and SEM were characterized. As shown in Fig. 2, the SEM images of MgAlO sample exhibited the flake-like structure, which were in accordance with literatures results [39]. However, the morphology was became massive texture when the copper was introduced, which might be due to the increase of the thickness of the hydrotalcite layers caused by the copper species entering into the laminate. The ICP-AES and BET data of the fresh and used 9%Cu-MgAlO were also summarized in Table 1. According to the data of surface area, pore volume, pore diameter and element content, it could be seen that the copper species of Cu-MgAlO catalyst were hardly leached after five runs, and the

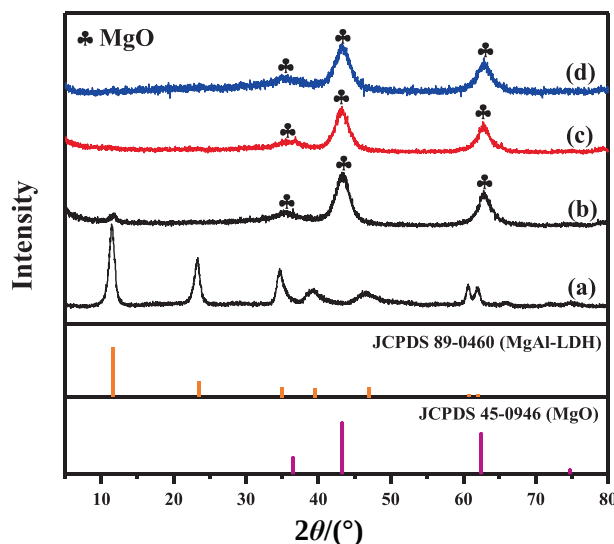


Fig. 1. XRD patterns of samples: (a) Cu-MgAl-LDH, (b) MgAlO, (c) fresh 9%Cu-MgAlO and (d) used 9%Cu-MgAlO.

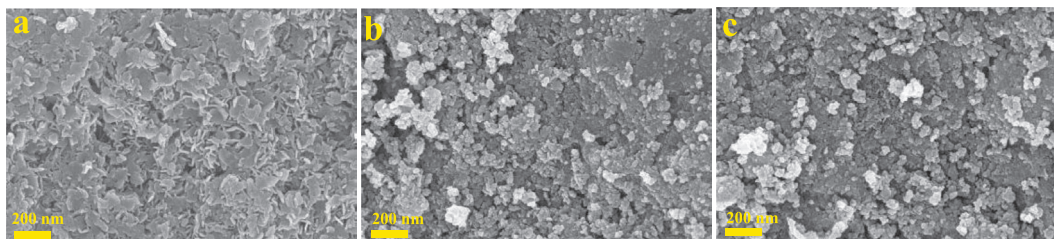


Fig. 2. SEM images of samples: (a) MgAlO, (b) fresh 9%Cu-MgAlO and (c) used 9%Cu-MgAlO.

Table 1

BET data and element contents of fresh and used 9%Cu-MgAlO catalysts

Catalyst	Element content/%			Surface area/m ² ·g ⁻¹	Pore volume/cm ³ ·g ⁻¹	Pore diameter/nm
	Cu	Mg	Al			
Fresh 9% Cu-MgAlO	9.50	32.89	17.64	107.80	0.40	21.50
Used 9% Cu-MgAlO	9.42	31.78	18.67	107.42	0.37	17.54

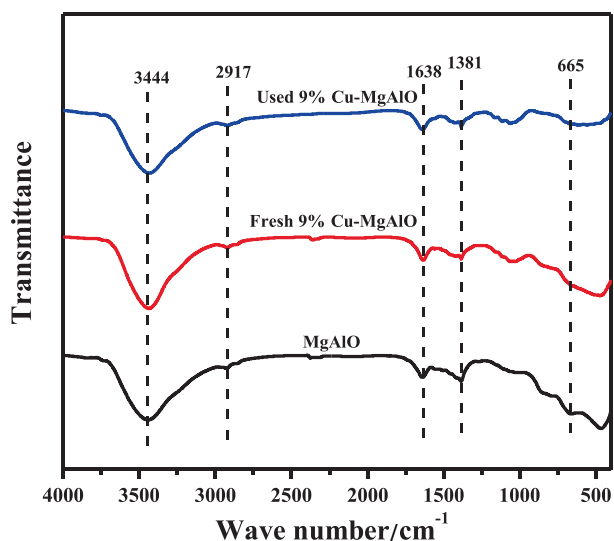


Fig. 3. FT-IR spectra of MgAlO, fresh and used 9%Cu-MgAlO.

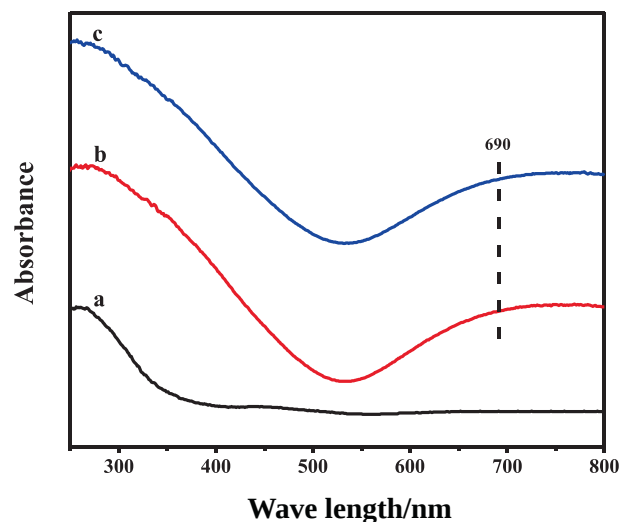


Fig. 4. UV-vis spectra of samples: (a) MgAlO, (b) fresh 9%Cu-MgAlO and (c) used 9%Cu-MgAlO.

textural properties of the catalyst were not obviously changed, which proved that the Cu-MgAlO catalyst displayed the good stability.

The FT-IR spectra of the samples were depicted in Fig. 3. All of these samples showed the similar infrared absorption characteristic peak. The IR absorption bands appeared at 3444 cm⁻¹ and 1638 cm⁻¹ were assigned to the O-H stretching vibration linked with the adsorbed and interlayer water [34]. The weak peaks at 2917 cm⁻¹ and 1381 cm⁻¹ were attributed to the ν_3 asymmetric stretching of trace CO₃²⁻ and stretching vibration of C-H bond, respectively [36,40]. The lower wave number band (665 cm⁻¹) and its vicinity were caused by various lattice vibrations associated with metal hydroxide sheets (HTlc) [41], which indicated that the copper was introduced to tetrahedral sites of the spinel oxides, and weakened the vibration absorption of metal oxides.

The UV-Vis DRS spectra of the catalysts were shown in Fig. 4. For MgAlO sample, no absorption peak was observed in the wavelength range of 500 to 800 nm. A wide absorption peak at 535–800 nm region could be seen for fresh 9%Cu-MgAlO sample, which contributed to electron d-d transitions of Cu²⁺ in a distorted octahedral surrounding by oxygen [42,43]. In addition, the UV-vis spectra did not change when the 9%Cu-MgAlO catalyst was used

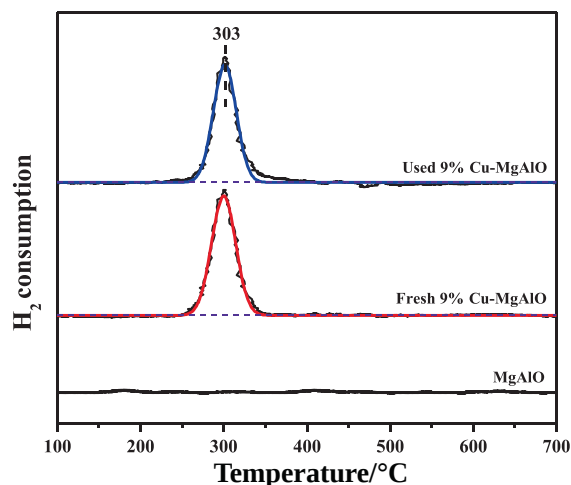


Fig. 5. H₂-TPR profiles of MgAlO, fresh and used 9%Cu-MgAlO.

in cyclohexane oxidation reaction, which was further testified the stability of the 9%Cu-MgAlO catalyst.

The reduction behavior of the catalysts were studied by H_2 -TPR characterization, and the results were displayed in Fig. 5. Clearly, the MgAlO sample showed no obvious reduction peak, indicated low reduction ability in the range at 700 °C. For the fresh and used 9%Cu-MgAlO samples, a single and strong H_2 -consumption peak presented at about 303 °C, assigning to the reduction process of Cu^{2+} to Cu^0 [43,44], which suggested that it existed in the form of Cu^{2+} species in 9%Cu-MgAlO sample. Moreover, the hydrogen consumption of used sample was similar to that of fresh 9%Cu-MgAlO. That was to say, copper species were not leached from 9%Cu-MgAlO catalyst during the oxidation process.

To investigate the valence state of copper species, the XPS characterization for fresh 9%Cu-MgAlO sample was carried out and the results were presented in Fig. 6. The survey scan spectrum showed photoelectron peaks due to Mg, Cu, O, Al at the binding energy positions of 1304 eV, 934.7 eV, 531.6 eV and 75.5 eV, respectively. The position of 284.6 eV was attributed to the signal peak of C as the substrate. To analyze the valence state of copper, the detail scan spectra of Cu 2p was further deconvoluted. Clearly, the peaks at binding energy positions of 934.4 eV and 954.5 eV were observed, which were assigned to $Cu^{2+} 2p_{3/2}$ and $Cu^{2+} 2p_{1/2}$ [45,46], respectively. In addition, the peaks at 942.6 eV and 962.4 eV were considered to the satellite peak accompanied by Cu^{2+} . These results testified the existence of Cu^{2+} species for fresh 9%Cu-MgAlO sample, which were consistent with those described in H_2 -TPR characterization.

3.2. Performance comparison of series catalysts for cyclohexane partial oxidation

Table 2 showed the catalytic performance of different Cu-MgAlO catalysts for the partial oxidation of cyclohexane. It could be seen that the reaction results of pure MgAlO were almost the same as that of the system without catalyst (Entries 1–2), which meant that the MgAlO showed low catalytic activity in the cyclohexane oxidation reaction. The catalytic activity was evidently enhanced as the transition metal (Mn, Fe, V or Co) was introduced to MgAlO. The conversion of cyclohexane was increased to 12.3% when the 9%V-MgAlO as the catalyst, but a lot of acids and esters were formed because of the strong oxidation of vanadium metal. When the 9%Mn-MgAlO and 9%Fe-MgAlO were used as catalysts,

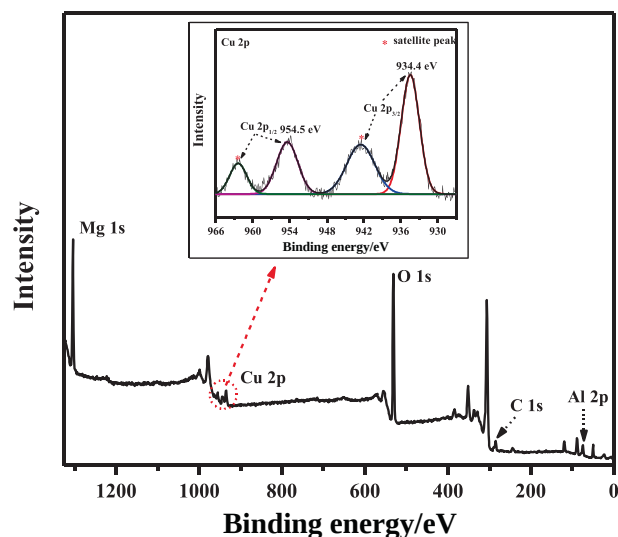


Fig. 6. Survey scan XPS spectrum and deconvoluted spectra of Cu 2p for fresh 9%Cu-MgAlO.

the selectivity of CHHP was exceeded 25%, while the selectivity of CHHP was decreased to 4.5% and the KA oil selectivity was improved to 82.9% over 9%Cu-MgAlO catalyst. This means that copper as the active species can absorb cyclohexane and activate the C–H bond, and it also can effectively decompose CHHP to KA oil. Moreover, the influence of copper loading for Cu-MgAlO catalysts was also investigated. The cyclohexane conversion was increased from 6.2% to 8.3% and the KA oil selectivity was increased from 71.1% to 82.9% with copper content elevated from 2% to 9%. This is due to the active copper species have a strong adsorption and activation effect on cyclohexane, and the catalytic performance gradually improves with the increase of copper loading. However, further raising the copper content to 18%, the catalytic performance was not further enhanced. The reason may be that the excess copper species will be aggregated, which are not conducive to the display of catalytic activity. Besides, in entry 7 for Table 2, we could see that the catalytic performance of simple physically mixed $CuO-MgO-Al_2O_3$ (the same mass percentage of copper as 9%Cu-MgAlO) catalyst were lower than the 9%Cu-MgAlO catalyst, which demonstrated that the textural properties of catalyst was closely correlated to its catalytic activity. Moreover, tert-butyl hydroperoxide as the additive was added in this reaction, the conversion of cyclohexane was improved significantly. On the contrary, radical inhibitor of *o*-dihydroxybenzene could stop the reaction. Therefore, the oxidation of cyclohexane with O_2 should be a free radical reaction.

3.3. Effects of reaction conditions for the cyclohexane oxidation with O_2 over Cu-MgAlO catalyst

Fig. 7 depicted the effects of reaction conditions for the oxidation of cyclohexane over 9%Cu-MgAlO catalyst. First, the effects of O_2 pressure in this reaction were shown in Fig. 7(a). Clearly, the cyclohexane conversion was increased gradually from 4.9% to 11.2%. However, the selectivity of KA oil increased to 82.9% and then decreased to 73.0%. The possible reason was that there were a series of competitive side reactions in the oxidation of cyclohexane, and the KA oil could be oxidized to generate propionic acid, butyric acid and other monobasic acids, and succinic acid, adipic acid and other dicarboxylic acids under high oxygen concentration. These acids would be further reacted with cyclohexanol to form corresponding esters. Fig. 7(b) presented the influence of reaction temperature for this catalytic reaction. Obviously, the conversion of cyclohexane was increased rapidly from 3.4% to 11.3% as raised the temperature from 140 °C to 160 °C, but the selectivity to KA oil was first elevated from 48.2% to 82.9% and then dropped gradually with the boundary of 150 °C. The reason might be that the activation of KA oil were likely to occur than activate cyclohexane at higher temperature because of difference of bond dissociation energies [47]. Therefore, the formation of a large number of acids and esters at higher temperature led to reduce the selectivity of KA oil. Fig. 7(c) showed the effects of reaction time on the oxidation reaction. It was clearly to be seen that the cyclohexane conversion was increased gradually while the KA oil selectivity was first increased and then declined with prolongation of reaction time. The selectivity of acid and ester was increased constantly might be due to the deep oxidation of KA oil in this process. Fig. 7(d) depicted the influence of catalyst dosage for the cyclohexane oxidation reaction. The conversion of cyclohexane and the selectivity of KA oil were increased steadily as raising of catalyst dosage from 0.01 g to 0.05 g. However, continuing to raised the amount of catalyst did not further increase the conversion and selectivity. This might be due to the excessive amount of catalyst was tended to be agglomerated, leading to hinder the improvement of the catalytic activity.

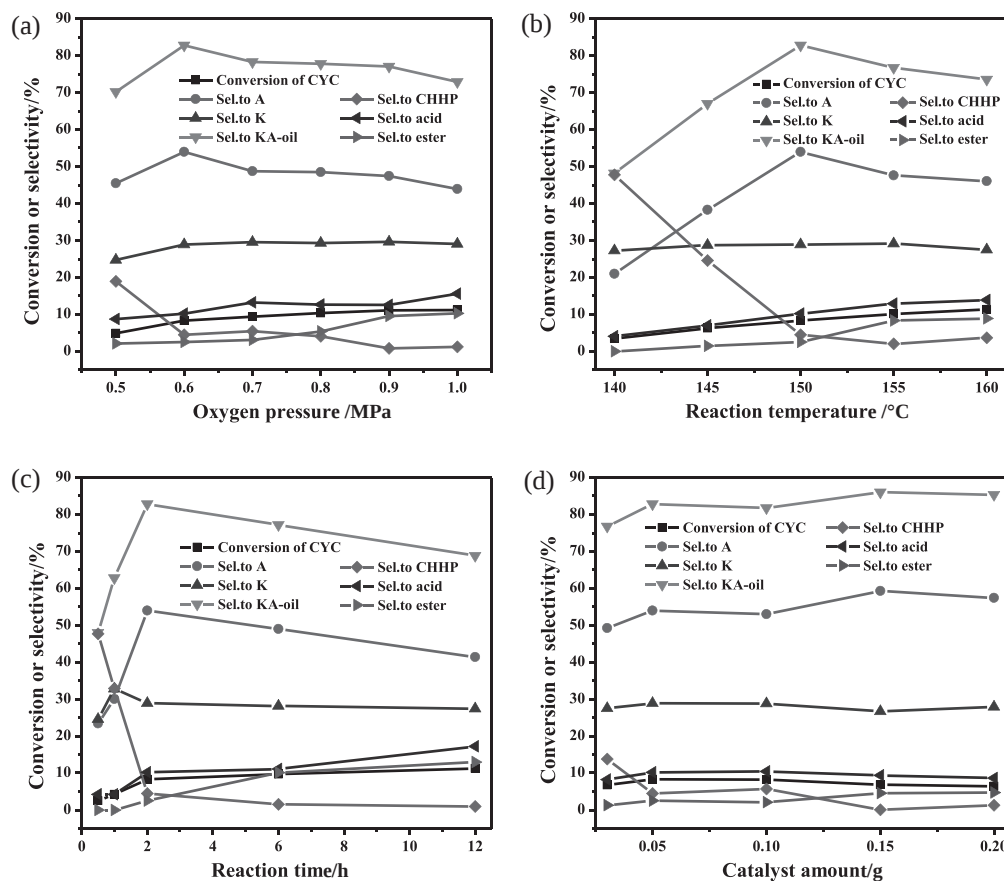
Table 2Performance comparison of series catalysts for cyclohexane partial oxidation with O₂

Entry	Catalyst	Conversion/%	Selectivity/%						TON ^①
			A	K	KA-oil	CHHP	Acid	Ester	
1	None	2.2	18.2	23.5	41.7	57.8	0.5	0	–
2	MgAlO	2.4	17.9	22.8	40.7	57.7	1.6	0	–
3	9%V-MgAlO	12.3	30.4	31.6	62.0	0	20.3	17.7	995.7
4	9%Mn-MgAlO	10.2	33.5	29.2	62.7	25.4	8.5	3.4	890.5
5	9%Fe-MgAlO	9.2	34.6	26.5	61.1	29.1	7.4	2.4	817.8
6	CuO	5.8	33.6	27.1	60.7	32.3	7.0	0	584.6
7	2%Cu-MgAlO	6.2	45.5	25.6	71.1	20.6	8.3	0	2812.1
8	4%Cu-MgAlO	7.0	49.0	26.0	75.0	14.7	8.2	0	1554.2
9	9%Cu-MgAlO	8.3	54.0	28.9	82.9	4.5	10.1	2.5	836.6
10	18%Cu-MgAlO	8.4	53.3	29.6	82.9	5.0	9.9	2.2	423.3
11	CuO-MgO-Al ₂ O ₃ ^②	8.1	45.6	31.7	77.3	5.5	10.9	6.3	816.4
12	None ^③	–	–	–	–	–	–	–	–
13	9%Cu-MgAlO ^③	–	–	–	–	–	–	–	–
14	9%Cu-MgAlO ^④	11.4	52.7	30.4	83.1	2.2	10.9	3.8	1149.0

Note: Reaction conditions are cyclohexane 60 g, catalyst 0.05 g, temperature 150 °C, oxygen pressure 0.6 MPa, reaction time 2 h.

① The turnover number (TON) = moles of products (CHHP + A + K + acid + ester)/moles of copper in the catalysts.

② Copper oxide, manganese oxide and aluminum oxide are physically mixed together.

③ Addition of *o*-dihydroxybenzene (3% (mass) of cyclohexane).④ Addition of *tert*-butyl hydroperoxide (3% (mass) of cyclohexane).**Fig. 7.** Influences of oxygen pressure (a), reaction temperature (b), reaction time (c) and the amount of catalyst (d) on the oxidation of cyclohexane over 9% Cu-MgAlO catalyst. (Standard reaction condition except the investigated parameter: 60 g cyclohexane, 0.05 g 9%Cu-MgAlO catalyst, 150 °C, 0.6 MPa O₂, 2 h).

3.4. Reuse and heterogeneity test of catalyst

The reusability of the Cu-MgAlO catalyst in the cyclohexane oxidation was tested at 150 °C with 0.6 MPa of O₂ for 2 h, and the results were shown in Fig. 8. Clearly, Cu-MgAlO catalyst showed the excellent reusability, an acceptable 8.0% of cyclohex-

ane conversion with 81.2% of selectivity toward KA oil was achieved after five runs.

The heterogeneous nature of Cu-MgAlO catalyst in the cyclohexane oxidation reaction was investigated by the hot filtration test. First, the catalytic reaction was carried out over 9%Cu-MgAlO catalyst at 150 °C and 0.6 MPa of O₂ for 1 h, then the reaction mixture

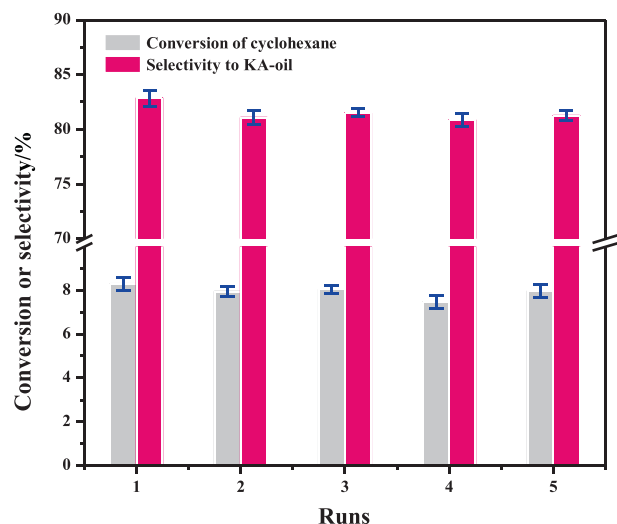


Fig. 8. The recycling results of 9%Cu-MgAlO catalyst for the cyclohexane oxidation with O_2 .

was taken out and filtered immediately to removed the catalyst. The obtained filtrate was returned to the reactor and continued to react for another 2 hours under the same reaction conditions. The results showed that the cyclohexane conversion was not further increased, which precluded the presence of active species in solution. Moreover, a part of filtrate was performed for the elemental analysis, no copper element was detected. Therefore, the oxidation of cyclohexane catalyzed by 9%Cu-MgAlO should belong to the heterogeneous reaction.

The catalytic performance of the prepared catalyst was compared to that of reported heterogeneous catalysts [9,48–55]. As shown in Table 3, although these catalysts such as $[CuCl_2\{HOCH_2C(pz)_3\}]$ and $[VCl_3\{HC(pz)_3\}]$ showed higher catalytic performance but lack in stability in the aerobic oxidation of cyclohexane. For example, 51.4% of cyclohexane conversion could be obtained when the Fe(TPPS)/pd-CTS catalyst was used for the first time, while the conversion of cyclohexane was reduced to 30.2% at the third use. In contrast, our catalyst system not only achieved good catalytic performance, but also maintained excellent stability in the oxidation of cyclohexane with O_2 .

3.5. Possible reaction mechanism of cyclohexane with O_2 to KA oil over Cu-MgAlO catalyst

It is well known that the oxidation of cyclohexane occurs through a free radical mechanism [9,48,55], and it has been

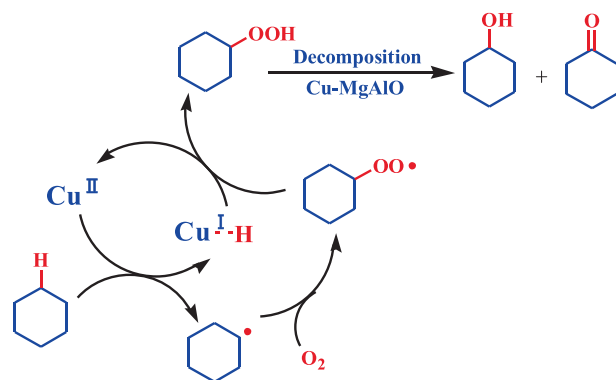


Fig. 9. Possible mechanism for cyclohexane oxidation over Cu-MgAlO catalyst.

demonstrated in our previous experimental results (entry 12 to 14 in Table 2). Moreover, the cyclohexyl hydroperoxide (CHHP) as a crucial intermediate existed in the initial stage of the reaction (Fig. 7(c)), and it was been decomposed into cyclohexanol and cyclohexanone with the extension of reaction time. Therefore, according to the obtained results in this work, the possible mechanism for the oxidation of cyclohexane with O_2 over Cu-MgAlO catalyst is proposed in Fig. 9. Initially, the cyclohexane was adsorbed and activated by copper species (Cu^{II}) to form cyclohexyl radical, which was reacted with O_2 to convert the cyclohexylperoxyl radical. Then, the formed cyclohexylperoxyl radical was desorbed from the active copper species (Cu^I) as CHHP, accompanied by the return of the active sites. Finally, the CHHP was decomposed to cyclohexanol and cyclohexanone under the catalysis of Cu-MgAlO catalyst.

4. Conclusions

In conclusion, a stable hydrotalcite-derived Cu-MgAlO mixed metal oxides catalyst was achieved by a simple co-precipitation method, which exhibited excellent catalytic performance for selective oxidation of cyclohexane toward KA oil. A series of characterization of the catalysts were carried out, and the obtained results proved that the copper oxides had been successfully introduced into the hydrotalcite unit layer structure. The catalytic reaction results indicated that copper as the active species could activate C–H bond and effectively decompose CHHP to KA oil. 8.3% conversion of cyclohexane and 82.9% selectivity to KA oil were achieved over 9%Cu-MgAlO catalyst under the optimal conditions. Maybe this catalyst can be extended to the other alkane partial oxidation to produce relevant alcohols and ketones.

Table 3

Comparison of reference catalysts with our catalyst system for cyclohexane oxidation with O_2 under solvent-free condition

Catalytic system	Reaction condition	Conversion/%	Selectivity (KA oil) /%
1. Mishra et al. [48]	$[CuCl_2\{HOCH_2C(pz)_3\}]$ catalyst, 1.0 MPa of O_2 , 150 °C, 4 h	13.7	84.9
2. Huang et al. [49]	Fe(TPPS)/pd-CTS catalyst, 0.8 MPa of O_2 , 155 °C, 4 h	51.4	55.8
3. Pomberio et al. [50]	$[VCl_3\{HC(pz)_3\}]$ catalyst, 1.5 MPa of O_2 , 140 °C, 18 h	13.3	92.5
4. Miao et al. [51]	The CoD(p-Cl)PPCl/ZnO catalyst, 1.5 MPa of O_2 , 155 °C, 5 h	11.0	84.3
5. Hutchings et al. [52]	AgPd/MgO catalyst, 0.3 MPa of O_2 , 140 °C, 17 h	9.5	78.0
6. Zhan et al. [53]	Ce-MCM-48 catalyst, TBHP as initiator, 1.0 MPa of O_2 , 140 °C, 4 h	8.9	91.2
7. Xu et al. [54]	Co_3O_4 nanocrystals catalyst, 1.6 MPa of O_2 , 145 °C, 6 h	7.6	89.1
8. Lu et al. [9]	$Mn_2Co_3O_8$ catalyst, 0.5 MPa of O_2 , 140 °C, 4 h	10.4	62.0
9. Corma et al. [55]	Au@MCM-22 catalyst, 1.0 MPa of O_2 , 150 °C, 2 h	near 13	near 78
10. This work	Cu-MgAlO catalyst, 0.6 MPa of O_2 , 150 °C, 2 h	8.3	82.9

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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