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Short Communication

CU^{II}(Sal-Ala)/MgAlLDH and CU^{II}(Sal-Phen)/MgAlLDH as novel catalytic systems for cyclohexene oxidation by H_2O_2

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ABSTRACT

We present here Cu^{II}(Sal-Ala)/MgAlLDH and Cu^{II}(Sal-Phen)/MgAlLDH complexes as novel catalytic systems for the cyclohexene oxidation by H_2O_2. The physical–chemical properties of the catalysts were investigated by XRD, FTIR, UV-Vis, XPS and TGA techniques. We present evidence that the properties of the Cu^{II}-based complexes and the specific properties of the LDHs matrix both beneficially contribute to establish the cyclohexene catalytic oxidation efficiency. Cu^{II}(Sal-Ala)/MgAlLDH showed the best catalytic activity with a cyclohexene conversion of 81% and 78% epoxide selectivity. The leaching effect of copper has not observed, and the CH epoxidation yields can be maintained during five catalytic cycles.

1. Introduction

The development of environmental friendly technologies has promoted sustained research for developing heterogeneous catalysis [1]. In particular, a high interest exists for designing novel catalysts for the partial oxidation of alkenes to produce epoxides that are flexible intermediate and precursor to many useful chemical products [2]. Various approaches have been focused on developing novel catalytic formulations by assembling metal-based catalysts onto various supports [3–7]. Mesoporous clay matrices, and especially layered double hydroxides (LDHs), are interesting to be used as supports in complex catalytic systems as they possess a unique combination of intercalation, swelling and exchange characteristics, which endows their ability to host on their surfaces or in the interlayer spaces various cationic species or complexes [8,9]. The catalytic systems based on transition metal complexes/LDHs are cheap, with a high compositional flexibility, environmental friendly and can be reused several times without loss of activity in, e.g., epoxidation reactions [8–11]. Cyclohexene epoxide is an important organic intermediate, and many efforts are devoted to find efficient and robust catalysts for epoxidation of cyclohexene using many metal catalysts [12–14]. Heterogeneous Schiff base complexes containing donor atoms such as oxygen and nitrogen have been used for oxidation reactions [15–20]. Sulfonato-salen-based catalysts can be intercalated in the interlayer spacing of LDHs, which leads to high activity and selectivity for epoxidation of various olefins [21]. A variety of copper-based reagents have been used as catalysts for selective oxidation of allylic compounds [20–24]. Amino acid Schiff base complexes that resemble the vitamin B6 amino acid catalytic enzyme have excellent catalytic performance for asymmetric synthesis and epoxidation [25].

In this work we present, from our knowledge for the first time, the Cu(II)-Schiff base complexes immobilized onto LDH supports as novel catalysts for cyclohexene oxidation. More precisely, the aims of this work have been (i) to synthesize Schiff base ligands derived from salicylaldehyde and alanine or phenylalanine amino acids and their Cu^{II} complexes; (ii) to immobilize the Cu^{II}(Sal-Ala) and Cu^{II}(Sal-Phen) complexes on the MgAlLDH (Scheme 1); and (iii) to evaluate the potential of thus prepared hybrid composites Cu^{II}(Sal-Ala)/MgAlLDH and Cu^{II}(Sal-Phen)/MgAlLDH as recyclable catalytic systems for the peroxidative cyclohexene oxidation.

2. Experimental

2.1. Materials

All chemicals were commercially purchased and used without further purification. $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Cu(CH_3COO)_2$ H_2O, Na_2CO_3, NaOH, salicylaldehyde, L-alanine, L-phenylalanine (Sigma-Aldrich) for the immobilized catalyst synthesis, cyclohexene (Aldrich) as substrate, H_2O_2 (Merck) as oxidant and methanol, ethanol, and acetonitrile as solvents were used in this study.

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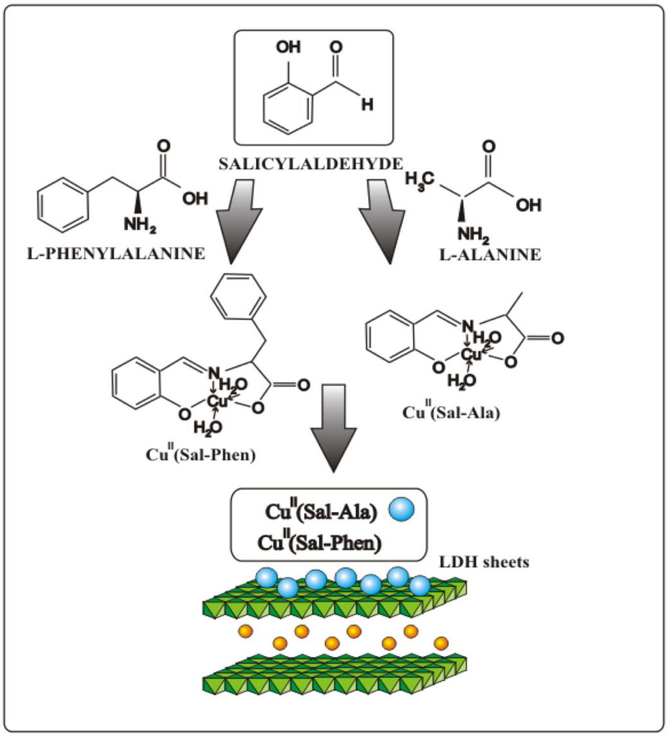

Scheme 1. Cu^{II}(Sal-Ala/Phen)/LDH catalytic systems.

2.2. Synthesis procedures

2.2.1. Preparation of LDH

The parent LDH was prepared by the pH controlled co-precipitation of the corresponding metal nitrate salts, followed by an ageing step of the synthesis medium at 45 °C for 24 h [5].

2.2.2. Synthesis of the metal complexes

The Cu^{II} complexes were synthesized as described in literature [25] and denoted Cu^{II}(Sal-Ala) or Cu^{II}(Sal-Phen). Alanine or phenylalanine (10 mmol) was added into a methanolic solution (50 mL) of NaOH (20 mmol). Salicylaldehyde (10 mmol) in 50 mL methanol and the copper acetate (5 mmol) were added and the mixture was kept under continuous stirring for 3 h at RT. The volume was reduced to 1/4 of the initial value, and the solid was filtered and recrystallized from a mixture of methanol-ethanol (2:1).

2.2.3. Cu^{II} Complexes/LDHs catalysts

The ethanolic suspension of 1 g MgAlLDH in 50 mL absolute ethanol with 0.5 mmol of metal complex was refluxed for 24 h with constant stirring and under nitrogen atmosphere. The final products (denoted Cu^{II}(Sal-Ala)/MgAlLDH and Cu^{II}(Sal-Phen)/MgAlLDH) were isolated by filtration, washed with bidistilled water then with acetonitrile and kept overnight in vacuum at 60 °C.

2.3. Physical–chemical characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker AXS D8 diffractometer by using Cu Kα radiation ($\lambda = 0.154$ nm) over a 2θ range from 3° to 70°. The FTIR spectra were recorded using a Bruker Alpha spectrometer. The UV-Vis diffuse reflectance spectra were recorded using a Thermo Scientific (Evolution 600) spectrometer. The copper content was determined by flame atomic absorption spectrometry (AAS) on a Spectra AA-220 Varian Spectrometer with an air-acetylene flame. C, H, and N contents were evaluated by combustion on a Fisons EA1108 elemental analysis apparatus. Thermogravimetric analysis (TG/DTA) was carried out in a Netzsch TG 209C thermobalance in nitrogen flow. The XPS spectra were obtained with a X-ray spectroscopy (ULVAC-PHI).

2.4. Catalytic epoxidation of cyclohexene

The epoxidation of cyclohexene (CH) was carried out in the liquid phase over Cu^{II} (Sal-Ala/Phen)/MgAlLDH using 30% H_2O_2 as the oxidant. The products were analyzed using a Thermo DSQ II system with gas chromatograph GC-Focus and mass spectrometer DSQ II.

H_2O_2 consumption was determined by an iodometric titration.

3. Results and discussion

3.1. Characterization of Cu^{II} complexes/LDHs catalytic systems

3.1.1. Elemental and energy dispersive X-ray analysis

Two Schiff base ligands derived from salicylaldehyde and alanine or phenylalanine amino acids and their Cu^{II} complexes have been synthesized and immobilized thereafter on the MgAlLDH support. Table 1 provides the data of elemental analysis. The chemical composition confirmed the purity and stoichiometry of the as-synthesized Cu^{II} complexes. The complexes are monomeric, being formed by the coordination of 1 mol of metal and 1 mol of Schiff base ligand. The greater amount of N% and C% for the hybrid composites might be a consequence of the presence of nitrate and carbonate anions in the interlayer of LDH even after the complexes immobilization, as the TG analysis has confirmed (Fig. 3).

Energy-dispersive X-ray analysis (EDX) of the immobilized complexes shows the metal content along with C, N, O, Mg and Al, suggesting the presence of the metal complexes on the LDH support surface (Table 2).

3.1.2. Powder X-ray diffraction

The XRD patterns of both immobilized Cu^{II} complexes and the LDH matrix (Fig. 1) are quite similar and exhibit some common features, such as narrow, symmetric, and strong peaks at low 2θ values and weaker, less symmetric lines at high 2θ values. For layered hydrotalcite-like materials, these peaks (0.74, 0.37 and 0.26 nm) correspond to diffraction by planes (003), (006), and (009), respectively. Hence, the overall structure of LDH is preserved upon the Cu^{II}(Sal-Ala/Phen) immobilization and is clear that newly formed hybrid composites are of Cu^{II}(Sal-Ala/Phen)/MgAlLDH type. This might indicates that the copper(II) complexes are immobilized on the surface or at the edges and/or defects of the crystal surface as indicated [26] for related systems.

3.1.3. FTIR, diffuse reflectance UV-Vis and XPS analyses

The coordination environment around Cu^{II} and the process of the complexes immobilization can be investigated using FTIR, UV-Vis and XPS analyses.

The characteristic bands indicating the successful preparation of the amino acid Schiff base complexes (Fig. 2(a)), namely, $\upsilon(C = N)$, $\upsilon_{as}(COO^-)$, $\upsilon_s(COO^-)$, υ(Cu-O) and υ(Cu-N), were all present in the FTIR spectra of the homogeneous complexes, and the band positions agree well with published data [27]. For the LDH support, the broad absorption between 3600 and 3300 cm^{-1} is due to the ν(OH) mode of the hydroxyl groups, both from the brucite-like layers and from interlayer water molecules. Interlayer water also gives rise to medium-intensity $\delta(H_2O)$ absorption close to 1628 cm^{-1}. The band at 1333 cm^{-1} is assigned to the stretching vibration of interlayer NO_3^-. The bands at wavenumber lower than 850 cm^{-1} are due to the M-O and O-M-O vibrations of the hydrotalcite [26]. In the FTIR spectra of the immobilized complexes, apart from the bands in the overlapping regions of the LDH support, only the $\upsilon_{as}(COO^-)$ band is clearly present

Table 1
Elemental analysis of Cu^{II}-Schiff base complexes free or LDH-supported.

Compound	Analytical data[a] (%)				Cu/N molar ratio	Immobilization yield, %
	C	H	N	Cu		
Cu^{II}(Sal-Ala),$C_{10}H_{13}NO_5Cu$	42.31 (41.21)	4.63 (4.47)	4.52 (4.80)	21.72 (21.80)	1/1	–
Cu^{II} (Sal-Ala)/LDH	6.66 (5.46)	1.86 (0.59)	3.58 (0.69)	2.86	1/6	90
Cu^{II}(Sal-Phen), $C_{16}H_{18}NO_5Cu$	52.65 (52.29)	4.98 (4.92)	3.62 (3.79)	17.28 (17.31)	1/1	–
Cu^{II} (Sal-Phen)/LDH	7.16 (5.76)	1.90 (0.54)	3.90 (0.42)	1.91	1/9	60

[a] Calculated values are shown in parentheses; for the immobilized complexes, the C%, H% and N% were calculated only for the ligand corresponding to the Cu% determined by AAS, considering a metal to ligand ratio of 1/1.

at 1563 cm^{-1} (see Fig. 2(a)) indicating the immobilization of the homogeneous complexes onto the LDHs.

The UV-Vis spectra of free and immobilized complexes are shown in Fig. 2(b). The UV-Vis spectra of the homogeneous complexes all displayed three typical peaks: at 250 nm due to benzenoid π-π^* transition, 380 nm assigned to a ligand-to-metal charge-transfer transition and the third peak around 600 nm associated with a *d-d* transition. The UV-Vis spectrum of Cu^{II}(Sal-Ala/Phen)/MgAlLDH showed similar features to the free complexes and to each other, indicating that during immobilization, no change of the Cu^{II} coordination center took place. However, the intensity of *d-d* transition band was lower due to the small amount of complex immobilized onto the LDH support.

The Cu2p XPS spectra (Fig. 2c) shown a main line at 932.9 eV that reflect a charge transfer metal $3d^{10}$ to ligand L^{-1}[28]. The electronic state of divalent copper compound is expressed by a resonance of ionic and covalent state. XPS data confirm the presences of copper only as complex on the surface of LDH support. A high percent of quaternary nitrogen atoms [29] was evidenced by XPS analysis (around 401 eV) revealing the presence of Cu^{II}(Sal-Ala) and Cu^{II}(Sal-Phen) complexes on the surface of LDHs. Further, the assignation of carbon peak at around 283 eV in XPS spectra with a large shoulder between 287 and 290 eV point out the presence o of carbon in $O = C$-OH and $-C = O$ compounds on the LDHs surface [30].

3.1.4. TG/DTA analysis

The thermal stability of MgAlLDH support and of the Cu^{II}(Sal-Ala/Phen)/MgAlLDH hybrid composites was studied and the TG curves are presented in Fig. 2.

In the thermal evolution of LDHs, the first two steps correspond to the removal of physically adsorbed and intergallery water (30–100 °C, 2.37% mass loss) and the dehydroxilation of the brucite-like layers (100–250 °C, 13.69% mass loss). The third weight loss (250–500 °C, 24.99% mass loss) is due to the decomposition of the nitrate anions [31]. The last step (500–900 °C, 4.57% mass loss) correspond to the LDH complete decomposition. Concerning the thermal decomposition of Cu^{II}-complexes/LDH, the sharp mass loss observed in the range 250–600 °C (29.20% mass loss for(Cu^{II} Sal-Ala)/LDH and 31.80% mass loss for Cu^{II}(Sal-Phen)/LDH, respectively) is due to the total dehydroxylation of the host layers, the decomposition of the organic guests and of the nitrate and carboxilate anions present in LDH interlayers. Furthermore, the mass losses calculated from TG curves are in accordance with the greater %C and %N determined by the elemental analysis. Considered together, the EDX, XRD, FTIR, DRUV, XPS and TG/DTA results show the formation of a new hybrid layered material by physical adsorption of the complexes onto the LDHs inorganic matrix, beside other weaker interactions such as hydrogen bonds, electrostatic interactions or donor–acceptor interactions between the complexes and the surface –OH groups [32,33] (Fig. 3).

Table 2
EDX measurements of LDH-supported Cu^{II}-Schiff base complexes.

	C	N	O	Mg	Al	Cu
Cu^{II} (Sal-Ala)/LDH						
Weight, %	10.64	0.34	59.28	17.07	9.11	3.56
Atomic, %	15.49	0.43	64.87	12.31	5.92	0.98
Cu^{II} (Sal-Phen)/LDH						
Weight, %	14.86	0.51	59.86	14.17	7.26	3.34
Atomic, %	20.90	0.61	63.21	9.84	4.55	0.89

3.2. Catalytic activity

3.2.1. Catalytic performances of the Cu^{II} complexes/LDHs

The catalytic activity of the studied LDH supported Cu^{II} Schiff base complexes was tested for the oxidation of CH at 60 °C, with H_2O_2 as oxygen source in acetonitrile as solvent. The solvent and LDHs joint effects arising from the clay surface and acetonitrile that would be interesting to the catalytic point of view. The reaction did not proceed in the absence of the catalyst and the CH conversion on pure LDH was very low (<6 mol% of max.). The results presented in Table 3 also show that the catalytic performance of the immobilized complexes is better than that of free complexes. The optimal CH conversion was 81% while the epoxide selectivity was 78% over Cu^{II} (Sal-Ala)/LDH, with an initial turnover frequency of 121 h^{-1}.

The higher CH oxidation values observed for the heterogeneous catalysts could be explained by the fact that the active centers are well isolated and separated from each other, which facilitate the epoxidation reaction. The enhanced catalytic performance of the immobilized

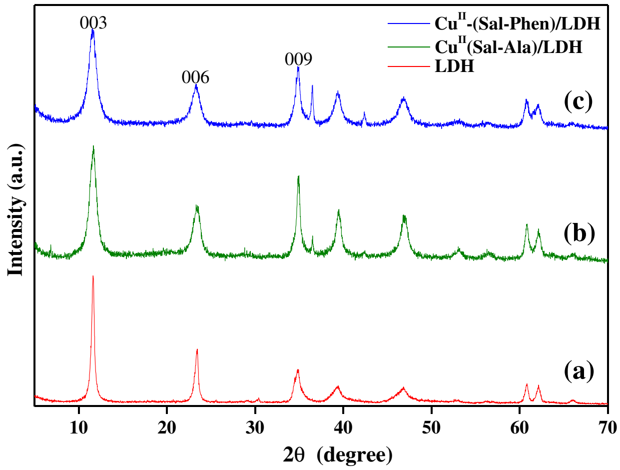

Fig. 1. XRD patterns of (a) LDH, (b) Cu^{II} (Sal-Ala)/LDH and (c) Cu^{II} (Sal-Phen)/LDH. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

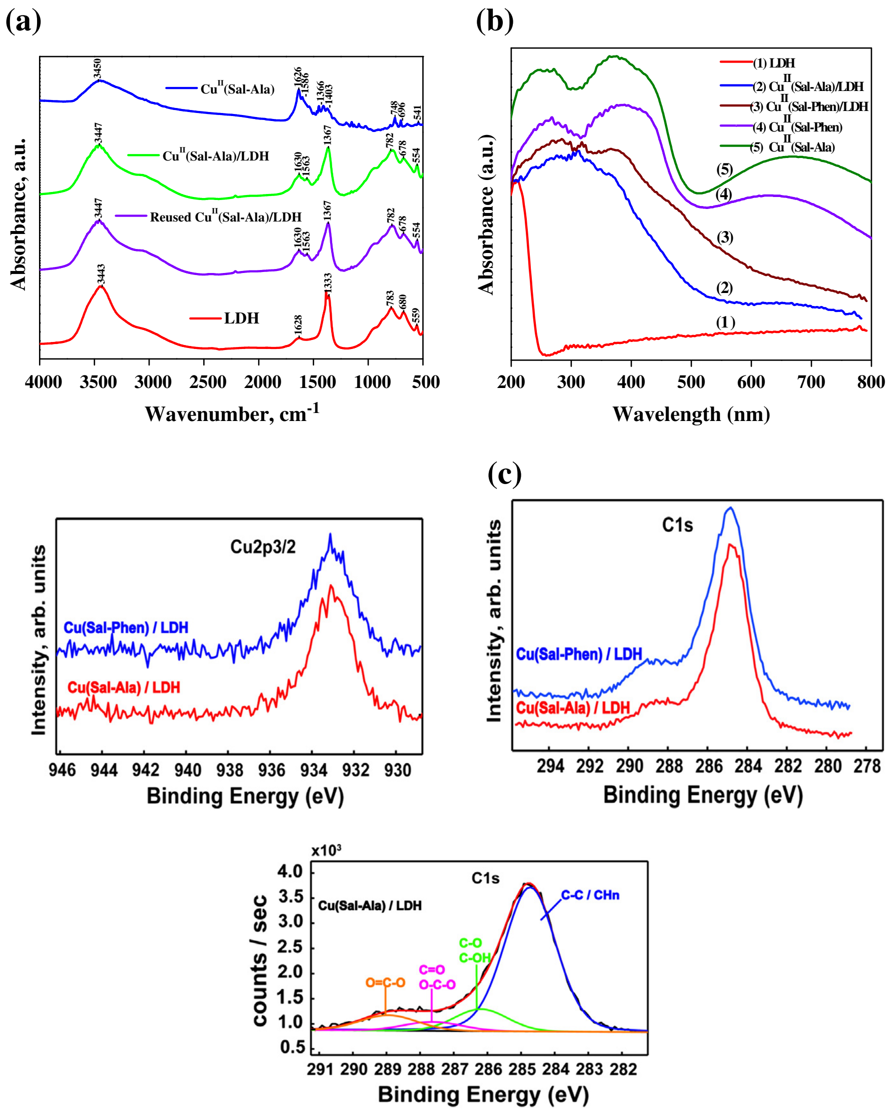

Fig. 2. FT-IR (a), UV-Vis (b) and high-resolution XPS spectra of Cu2p 3/2, C1s and C1s deconvoluted (c) for free complexes and Cu^{II}(Sal-Ala/Phen)/LDH. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

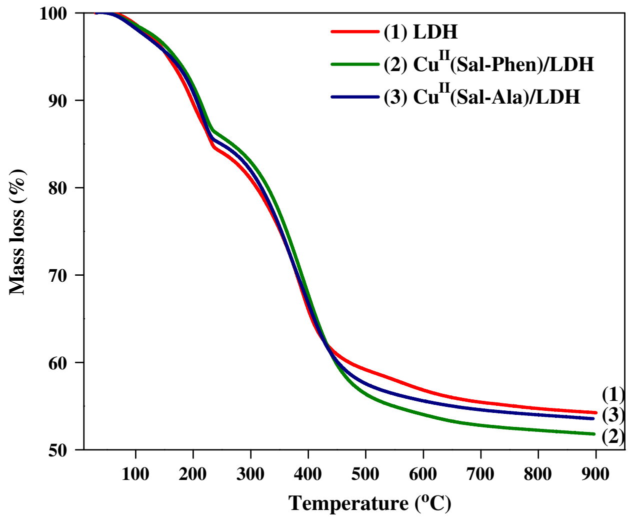

Fig. 3. TG curves of (a) LDH, (b) Cu^{II} (Sal-Ala)/LDH, (c) Cu^{II} (Sal-Phen)/LDH. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

complexes is linked to the supported LDH matrix by modification of the local environment of the active sites and of the local concentrations of the reactant and the products around the active sites [27]. The LDH support allow a better control of metal ions interactions with the substrate in the intermediates and facilitate the formation of reaction

Table 3
Catalytic performance of the different copper complexes.

Sample	CH conversion (%)	TOF (h^{-1})	Selectivity (%)		
			I	II	III
Cu^{II} (Sal-Ala)	18	18	68	22	10
Cu^{II} (Sal-Phen)	22	33	70	21	9
Cu^{II} (Sal-Ala)/LDH	81	121	78	13	9
Cu^{II} (Sal-Phen)/LDH	57	86	83	12	5

Reaction conditions: catalyst (50 mg), substrate (2.26 mmol), ACN (10 mL), H_2O_2 (4.75 mmol), 5 h, 60 °C,
Products formed: cyclohexene oxide (I), 2-cyclohexen-1-ol (II) and 2-cyclohexen-1-one (III);
CH conversion (%) = [CH converted (moles) / CH used (moles)] × 100.
Product selectivity (%) = [product formed (moles) / total product detected (moles)] × 100.
TOF = Substrate converted (moles) / [Copper in catalyst (moles) × reaction time (h)]; t = 20 min.

products through an easiest route of energy surfaces compared to unsupported complexes. The surface nature of the LDH support have an important contribution to establish the catalyst selectivity as the base strength of the catalyst is essential for the selective conversion of CH to the corresponding epoxide. In our case, a synergetic effect due to the presence of both base sites and copper metal sites was observed.

Considering that the immobilized complexes own a similar surface polarity and hydrophobicity, the significant differences in their catalytic performance could be reasonably attributed to their different metal loading and ligand structures.

In the present reaction system, the CH oxidation is accompanied by the side reaction of self-decomposition of H_2O_2 [26]. The effective utilization of H_2O_2 was found to be 61% for Cu^{II}(Sal-Ala)/LDH and 54% for Cu^{II} (Sal-Phen)/LDH, respectively. The main products obtained during cyclohexene oxidation are cyclohexene oxide (I), 2-cyclohexen-1-ol (II) and 2-cyclohexen-1-one (III). According to GC–MS analyses, the products mixture is composed of species formed by oxidation of both double bond and allylic C–H. Based on the greater epoxide selectivity for both tested catalysts, it is clear that the activated oxygen insertion across $C = C$ double bond of cyclohexene yielding cyclohexene oxide is the principal reaction.

Comparing the CH conversion and epoxide selectivity of these catalysts with a Cu–Salen complex immobilized on KIT-6 mesoporous silica [14] and used for CH oxidation with H_2O_2 in ACN at 70 °C or with Mn, Fe-sulfonato-salen catalysts hosted in LDH and used for the CH epoxidation with pivaldehyde and molecular oxygen, [34] these new catalysts present both higher conversion and better epoxide selectivity. However, a Ti(IV)-Schiff base complex intercalated into LDH presented a 95% CH conversion, and 84% epoxide selectivity, at 70 °C, using H_2O_2 oxidant, without solvent [26].

3.2.2. Effect of the reaction conditions on the catalytic performance of the immobilized complexes

First, the effect of the H_2O_2/C_6H_{10} molar ratio on CH conversion and epoxide selectivity was investigated when the reaction run for 5 h at 60 °C with a Cu^{II}(Sal-Ala)/MgAlLDH catalyst dose of 0.05 g in 10 mL acetonitrile solvent (Fig. 4(a)). These results suggest that 2.2:1 molar ratio is the minimum requirement for the effective oxidation of CH along with the best epoxide selectivity and better percentage H_2O_2 efficiency.

The effect of the amount of catalyst on the catalytic performance was investigated (Fig. 4(b)). At the beginning of the reaction CH conversion and epoxide selectivity both increased with an increase in the amount of catalyst until 0.05 g. As the catalyst amount increased, the % H_2O_2 decomposition will increase which in turn decrease the oxidation process i.e. lower conversion.

Concerning the effect of the reaction temperature on the epoxidation reaction (Fig. 4(c)), the CH conversion was found to increase significantly from 40% at 30 °C to 81% at 60 °C. In the reaction conditions as far optimized, the influence of reaction time on the reaction was further investigated (Fig. 4(d)). The results reveal that the epoxidation reaction is a fast reaction that presents a sharp increase of CH conversion after 1 h run. With a further increase in the reaction time, the epoxidation reaction reached maximum yield of epoxide after 5 h.

In conclusion, the best operation parameters for CH selective oxidation to epoxide were 5 h reaction run at 60 °C with 0.05 g catalyst, 10 mL solvent and a 2.2/1 H_2O_2/C_6H_{10} molar ratio.

3.2.3. Stability of Cu^{II} complexes/LDHs in the process of cyclohexene epoxidation

For the Cu^{II}(Sal-Ala)/MgAlLDH heterogeneous catalyst, the stability under the optimum reaction conditions was further investigated by

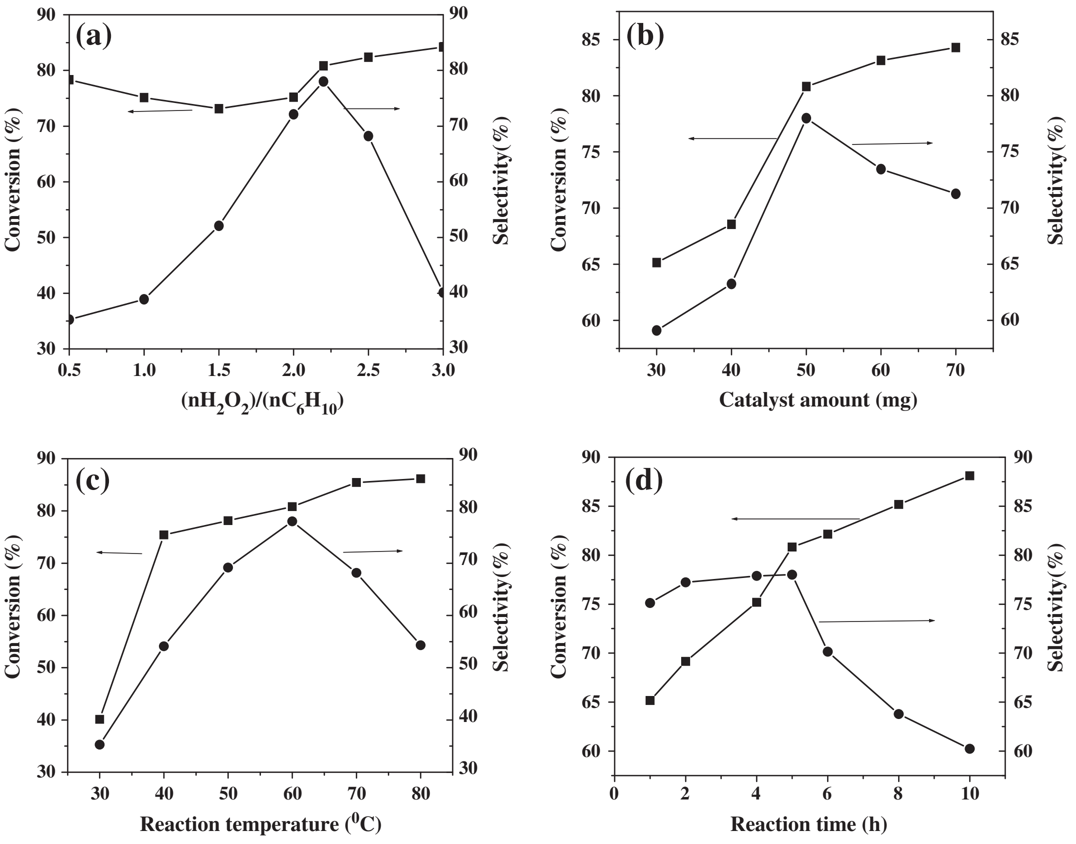

Fig. 4. Effects of condition parameters on the catalytic performance of the immobilized complexes. Reaction conditions: substrate (2.26 mmol), ACN (10 mL). (a) H_2O_2/C_6H_{10} molar ratio: catalyst (50 mg), 60 °C, 5 h; (b) amount of catalyst: $H_2O_2/C_6H_{10} = 2.2/1$, 60 °C, 5 h; (c) reaction temperature: catalyst (50 mg), $H_2O_2/C_6H_{10} = 2.2/1$, 5 h; (d) reaction time: catalyst (50 mg), $H_2O_2/C_6H_{10} = 2.2/1$, 60 °C.

Table 4
Catalytic reusability.

No. of cycle	CH conversion %	Epoxide selectivity %	Initial TOF (h^{-1})
1	81	78	121
2	77	73	100
3	68	63	85
4	63	57	63
5	59	53	54

measurements of initial reaction rates and conversions over five cycles [1c]. The catalyst was still active during the fifth run, but the initial TOF was diminished (Table 4). AAS measurement results revealed that the recovered catalyst almost had the same copper content as the fresh catalyst (Cu, 2.82%) and in the FTIR spectrum (see Fig. 2(a)) no significant change was observed. This further indicates that the obtained LDH hosted copper complexes were stable and the leaching of the metal complexes was not the main reason for the decreased catalytic performance. The changes of the nature of the active species in the oxidizing medium might gives rise to catalysts deactivation. Further, the adsorption of the reaction products on the support may also produce a limitation in the substrate diffusion with an increase in number of cycles. Further work will be focused to improve the catalyst stability. Results indicate that the thermal treatment is excellent for reusing the catalyst in CH epoxidation [35]. It should be underlined that the recyclable heterogeneous catalysts developed in this study are obtained by a cheaper and facile procedure, more convenient that most procedures used to develop related catalytic systems reported in literature for CH oxidation catalytic processes [12,14,31].

4. Conclusions

Novel catalysts based on Cu^{II}(Sal-Ala/Phen) complexes supported on MgAlLDH matrices were prepared and tested in the process of epoxidation of cyclohexene with 30% H_2O_2.

The immobilization of Cu(II)-based complexes on the LDH support beneficially contributed to the catalytic performances. Moreover, Cu^{II} complexes/MgAlLDHs catalysts are easily recyclable and can be reused at least five times. The leaching effect of copper was not observed and the CH epoxidation yields can be maintained. The obtained results can pave the way for the development of highly effective heterogeneous catalysts, obtained by the immobilization of metal complexes into the LDH matrices, for the efficient epoxidation of cyclohexene.

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