Synthesis and characterization of a Fe(III)-Schiff base complex in a Zn-Al LDH host for cyclohexane oxidation

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ABSTRACT

The paper reports the synthesis, characterization and catalytic evaluation of a Fe(III)-Schiff base complex intercalated Zn-Al layer double hydroxide (LDH). The immobilized complex was characterized by powder X-ray diffraction, FT-IR, UV–vis spectroscopy, N_2 adsorption desorption, scanning electron microscopy and TGA techniques. The immobilization complex was found to be an effective catalyst for oxidation of cyclohexane using H_2O_2 as an oxidant under mild conditions. A conversion of 45.5% of cyclohexane was obtained with selectivity of 100% of the cyclohexanone/cyclohexanol at 70 °C in 8 h in acetonitrile solvent. Recycling test of the catalyst showed that it was recovered and reused up to 3 more cycles without loss of performance.

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1. Introduction

Layer Double Hydroxides (LDHs) being typical intercalation compounds are of considerable interest due to their valuable and unique ion exchange intercalation properties [1–5]. It has the general formula $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+} (A^{n-})_{x/n} \cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metals respectively and A^{n-} is the anion which compensates for the positive charges of the metal hydroxide layers. LDH that afford space between the layers are found to be a suitable host for intercalation of planar transition metal complex catalyst containing porphyrin, phthalocyanine or Schiff base ligands [6–11]. The development of environmental friendly technologies have promoted much research in heterogeneous catalysis and in particular the heterogenization of known active homogeneous catalysts for oxidation [12,13]. Schiff base ligands derived from an aldehyde and amine, and their complexes with transition metals have been widely used in many organic transformations. Papers dealing with immobilizations of these complexes within mesoporous supports have been extensively studied [14,15]. However studies on the intercalation of transition metal complexes into hydrotalcite layers are rather limited. Oxidation of cyclohexane has been extensively studied using homogeneous Mn(III), Fe(II) and Fe(III) complexes [16–18]. But the problem arises due to its separation method and reuse makes it utilization rather limited. It has been claimed that LDH-hosted catalysts do not suffer from leaching of the active metal in epoxidation reactions and that they can be reused several times without loss of activity [19,20]. These findings prompted us to test the efficacy of a LDH-hosted Fe(III)-Schiff base complex as a catalyst for oxidation of cyclohexane.

Oxidation of relatively inert C–H bond of hydrocarbons constitute one of the most desirable and challenging reactions due to large demands of its oxidized products [21,22]. The selective oxidation of cyclohexane is an industrially important reaction because of its oxidized products such as cyclohexanol and cyclohexanone, which are important intermediates in the production of adipic acid and caprolactam. Caprolactam is used in manufacture of Nylon-6 and Nylon-66 polymers. In current industrial process, cyclohexane is oxidized at a temperature range of 150–170 °C and pressure of 115–175 psi in presence of homogeneous cobalt salt, where the conversion is very less (∼4%) and the process is environmentally hazardous [23,24]. The development of catalysts that do not expend too much energy and that utilize oxidants less harmful from an environmental standpoint is generally preferred. From this aspect H_2O_2 is chosen to a better oxidant than dioxygen insofar as O_2–organic mixture sometimes ignites [25].

In our present work we have made homogeneous Fe(III)-Schiff base complex to heterogeneous catalysts by immobilization into LDH. The Fe(III)-Schiff base loaded LDH showed good catalytic activity towards cyclohexane oxidation by using H_2O_2 as oxidant. The catalyst is regenerable and reusable for oxidation of cyclohexane.

2. Experimental

2.1. Materials

$Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, acetonitrile (s.d. Fine Chemicals), cyclohexane, salicylaldehyde (Qualigen),

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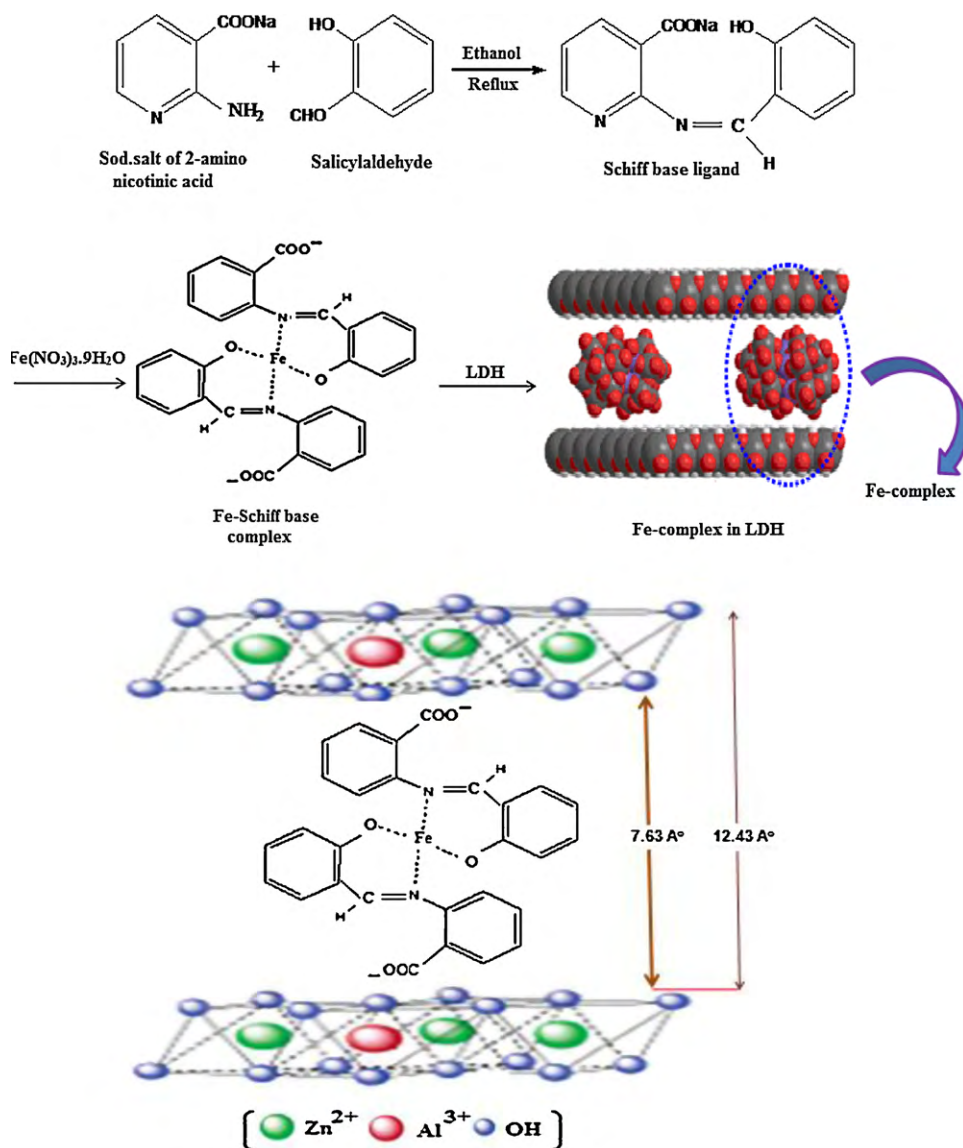
Scheme 1. Schematic representation for preparation of LDH/Fe complex.

cyclohexanone, cyclohexanol (Sigma–Aldrich), 2-amino nicotinic acid (Across) were used without further purification.

2.2. Synthesis procedures

2.2.1. Preparation of LDH

The layer double hydroxide containing Zn-Al with Zn:Al molar ratio 3:1 was prepared by the co-precipitation method at a constant pH [26]. The synthesis was carried out by the slow addition of mixed metal nitrate solution (1 M in total) $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ to a 2 M NaOH solution under magnetic stirring. During the synthesis the pH of the solution was found to be 11. The resulting slurry was kept stirring for 1 h at room temperature. Then it was filtered, washed thoroughly with deionized water till the washings were neutral and dried at 100 °C overnight.

2.2.2. Synthesis of the metal complex

2-Aminonicotinic acid upon treated with Na_2CO_3 produce the sodium salt of 2-aminonicotinic acid. Equimolar amount of sodium salt of 2-aminonicotinic acid and salicylaldehyde were refluxed in ethanolic solution to produce a Schiff base ligand. The iron complex

was formed by refluxing 0.484 g (2 mmol) Schiff base ligand and 0.404 g (1 mmol) $Fe(NO_3)_3 \cdot 9H_2O$.

2.2.3. LDH/Fe Complex

1 g of LDH (Zn/Al) was dried under reduced pressure at 100 °C. To an ethanolic suspension of 1 g LDH, the whole metal complex was transferred and refluxed for 24 h. After filtration the final product was abbreviated as LDH/Fe complex. The total schematic representation for the synthesis of LDH/Fe complex is depicted in Scheme 1. Atomic absorption spectrometric analysis showed iron content in the LDH/Fe complex is c.a. 0.32%.

2.3. Physico-chemical characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX2500 diffractometer, using Cu Kα radiation at 40 kV, 30 mA, a scanning rate of 5°/min, and a 2θ angle ranging from 3° to 80°. The FT-IR spectra of the samples were recorded using Varian 800-FT-IR in KBr matrix in the range of 4000–400 cm^{-1}. The coordination environments of the samples were examined by diffuse reflectance UV–vis spectroscopy. The spectra were recorded
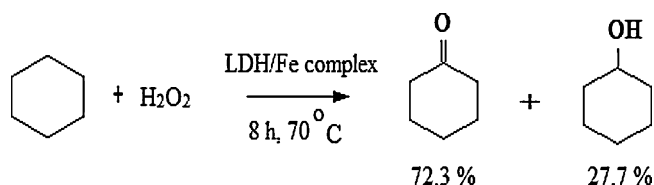
Scheme 2. Catalytic oxidation of cyclohexane.

in Varian-100 spectrophotometer in the wavelength range of 200–800 nm in $BaSO_4$ phase. Surface area was determined by nitrogen adsorption–desorption at liquid nitrogen temperature (77 K) using ASAP2020 (Micromeritics). Prior to adsorption–desorption measurement the samples were equilibrated by degassing at 120 °C for 6 h. SEM images were obtained using HITACHI 3400N microscope. Thermogravimetric analysis (TGA) was performed under air with a Shimadzu TGA-50 system at a heating rate of 5 °C min^{-1}. The Fe loading in the catalyst and in the leaching solution was determined by atomic absorption spectroscopy (AAS) with a PerkinElmer Analysis 300 using acetylene (C_2H_2) flame.

2.4. Catalytic reaction

The typical catalytic oxidation of cyclohexane (Scheme 2) was carried out as follows: 18 mmol of cyclohexane, 0.05 g of catalyst and 10 ml of acetonitrile were added successively in to a temperature controlled two-necked round-bottom flask with a reflux condenser. Then 18 mmol of hydrogen peroxide (H_2O_2) was added drop wise. Reaction was carried out for 8 h at 70 °C. After completion of the reaction, it was filtered and the products of the mixture were analyzed offline by GC-2010 (Shimadzu) equipped with a capillary column (ZB-1, 30 m length, 0.53 mm I.D. and 3.0 μm film thickness) using flame ionization detector (FID). Calculation for self-decomposition (SD), conversion and selectivity (SE) of H_2O_2 were given below.

Self-decomposition (SD) of H_2O_2 = volume of oxygen released in the reaction.
Conversion of H_2O_2 = consumption of H_2O_2 (including self-decomposition)/initial amount of H_2O_2.
Selectivity (SE) of H_2O_2 = H_2O_2 consumption for product formed/total consumption of H_2O_2.

The decomposition of H_2O_2 was followed by measuring the volume of oxygen liberated at atmospheric pressure by conventional gasometric method [27].

3. Results and discussion

3.1. Characterization of the heterogeneous catalyst

3.1.1. Powder X-ray diffraction

Fig. 1 shows the XRD patterns of LDH (a) and LDH/Fe complex (b). The expected $d(0\,0\,3)$ peak characteristics of the diffraction pattern of layered materials was recorded. The XRD pattern of LDH-NO_3 shows a basal reflection at 8.67 Å, which is similar to that reported in the literature [28]. In case of complex intercalated LDH the basal spacing increases from 8.67 Å to 12.43 Å. The gallery height of the intercalated materials is 7.63 Å. The increase in gallery height strongly suggests the successful intercalation of Fe(III)-Schiff base complex. The XRD pattern indicates that the layered structure is maintained and that the basal spacing in the intercalated materials depends on the transition metal complex [29]. In comparison to parent LDH, (0 0 3) reflection of the complex intercalated LDH shifted to lower 2θ value. This corresponds to an increasing
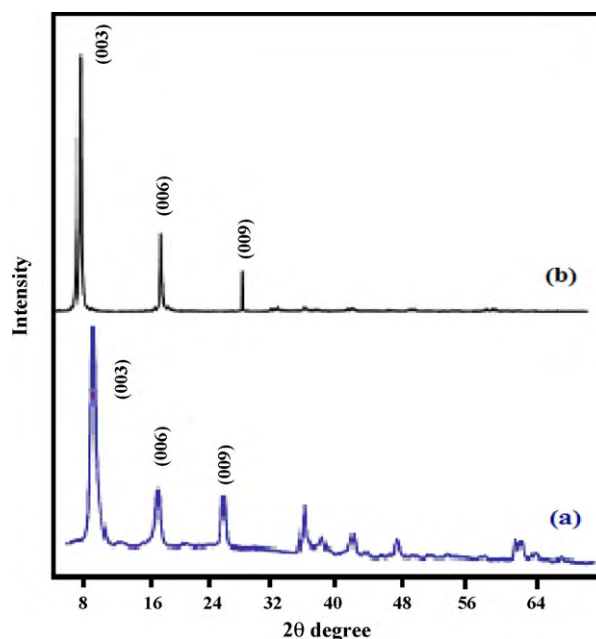

Fig. 1. XRD patterns of (a) LDH and (b) LDH/Fe complex.

interlayer distance which is a direct indication of Fe(III)-Schiff base complex in the interlayer space of LDH.

3.1.2. FT-IR studies

FT-IR spectra of (a) LDH (b) Fe complex and (c) LDH/Fe complex are shown in Fig. 2. For the sake of clarity we have indicated some of the important bands in our figure. The spectrum of LDH precursor shows an intense and broad absorption band at 3490 cm^{-1} is due to the stretching vibration of the hydroxyl group in the LDH layers and interlayer water molecules [29]. The broadening of the band is due to hydrogen-bond formation. The band at 1384 cm^{-1} is assigned to the stretching vibration of interlayer NO_3^-. The bands around 445 and 675 cm^{-1} are due to Al-O and Zn-O lattice vibrations respectively. Fe complex is showing all possible characteristics bands in their corresponding regions due to Schiff base. Bands at 1640 and 1725 cm^{-1} are due to C=N stretching of imine group and C=O stretching of carboxylate group respectively. 3450 cm^{-1} may be due to some uncoordinated –OH groups of phenyl ring. In case
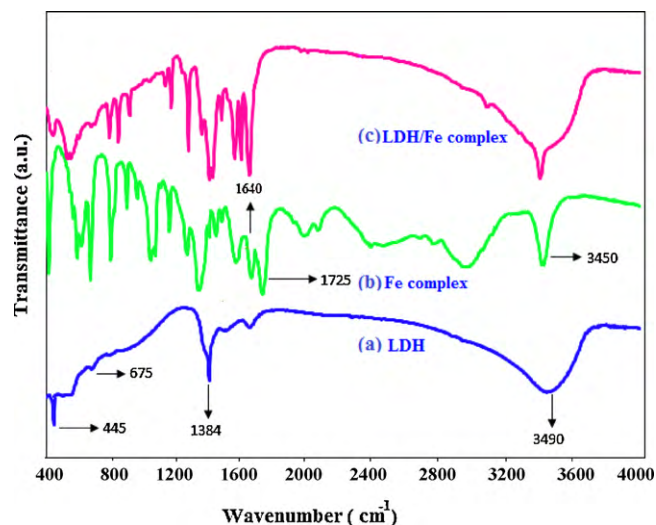

Fig. 2. FT-IR spectra of (a) LDH, (b) Fe complex and (c) LDH/Fe complex.
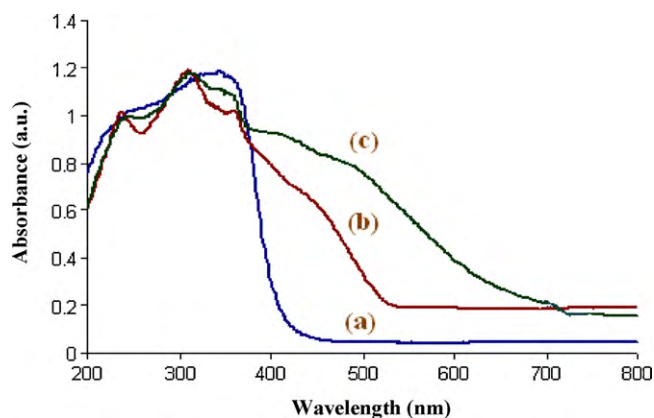
Fig. 3. Diffuse reflectance spectra of (a) LDH, (b) Fe complex and (c) LDH/Fe complex.

Fig. 4. N_2 adsorption–desorption isotherms of (a) LDH and (b) LDH/Fe complex.

of LDH/Fe complex a sharp and merge band around 3450 cm^{-1} appears, may be due to overlap of bands of hydroxyl group of brucite layers and uncoordinated –OH groups. All the above results indicate intercalation of Fe(III)-Schiff base complex in the interlayer space of LDH.

3.1.3. Diffuse reflectance UV–vis spectral studies

The electronic spectra of LDH, Fe complex and LDH/Fe complex were recorded and shown in Fig. 3. The absorption bands at 260 and 320 nm may be assigned to a Schiff base to metal ion charge transfer band (LMCT). Earlier studies reported similar band spectra in this region for Fe(III)-salen complex [30]. Fe complex showed broad band in the region of 480 cm^{-1} due to d–d transition of Fe(III) [31]. The UV–vis spectrum of LDH/Fe complex showed similar features to the free complex, indicating that during intercalation no change of the Fe(III) coordination center took place.

3.1.4. N_2 adsorption–desorption studies

N_2 adsorption–desorption isotherm at 77 K for LDH and LDH/Fe complex are shown in Fig. 4. Complex intercalated LDH shows higher surface area compare to neat LDH. The reason is that when bigger complex molecules are incorporated into the LDH layers, the expansion took place (i.e. increase in basal spacing from 8.67 Å to 12.43 Å). As a consequence of which surface area of LDH/Fe complex increases from 84 to 129 m^2/g.

3.1.5. SEM studies
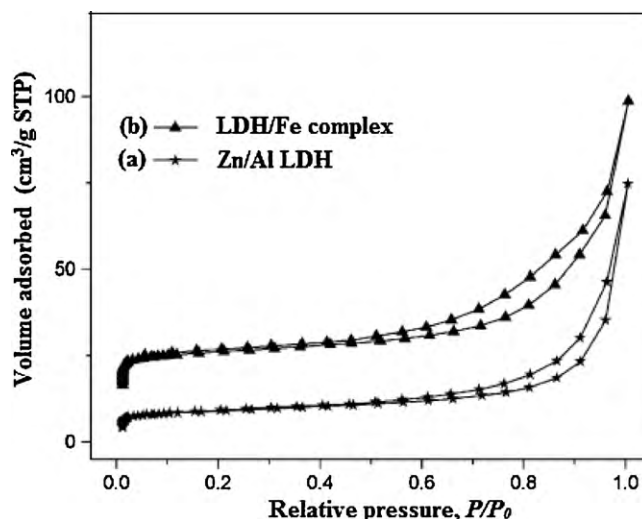
Fig. 5 shows scanning electron micrographs of each of the catalysts prior to the reaction. The unmodified LDH has a rose-petal like aggregates of planar sheets morphology with sharp edges. But in case of complex intercalated LDH a slight sheet deformation images indicates intercalation of complex in the ion exchange process.

3.1.6. TGA studies

Fig. 6 shows the thermo gravimetric analysis curves for Zn/Al LDH (solid line) and LDH/Fe complex (dotted line), which shows the thermal decomposition behavior. The first weight loss for Zn/Al LDH occurs from room temperature to 125 °C and is due to the removal of crystallization water (7%). A mass loss of 28.4% then takes place in the temperature range 200–500 °C, attributed to decomposition of the brucite-like layer and removal of interlayer anions. The water content in LDH/Fe complex is higher as evidenced by a mass loss of 14.5% extending from room temperature to 160 °C. A second step is observed from 175 to 230 °C, assigned to partial dehydroxylation of the double hydroxide layers. Complete dehydroxylation of the lattice takes place from 390 to 550 °C, accompanied by elimination/decomposition of the organic anions.
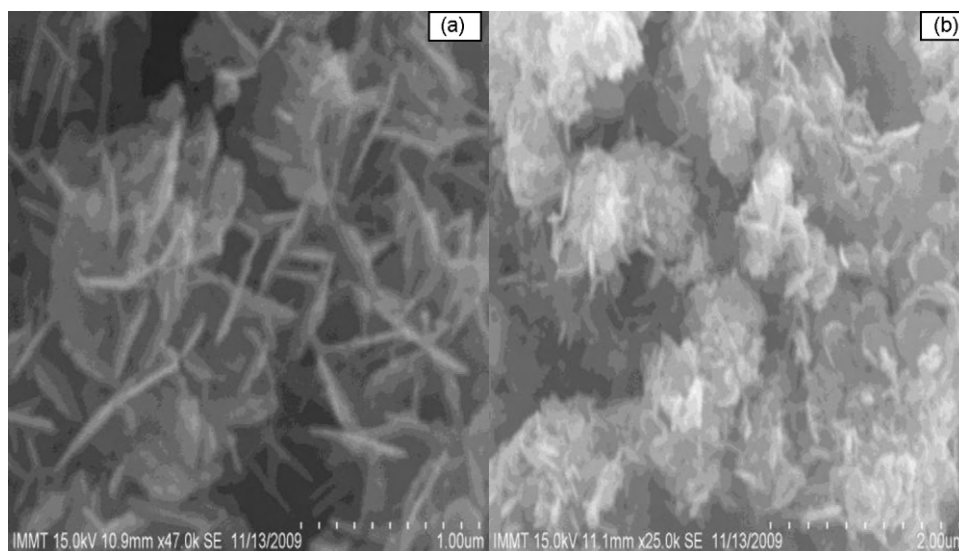

Fig. 5. SEM images of (a) LDH and (b) LDH/Fe complex.

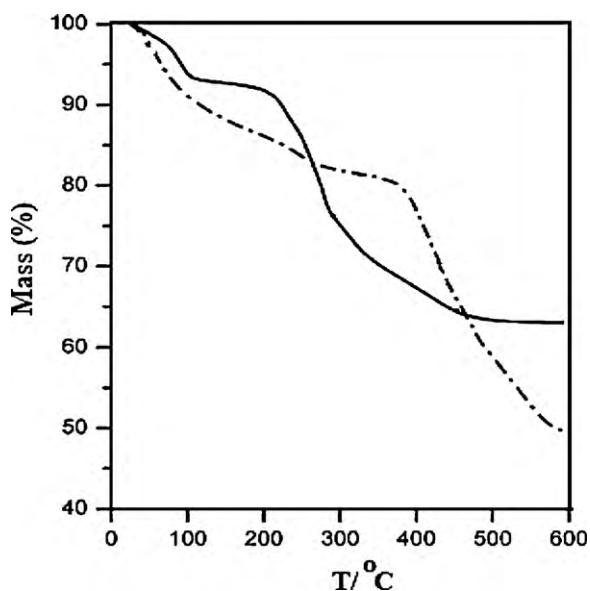**Fig. 6.** TGA curves of Zn/Al LDH (solid line) and LDH/Fe complex (dotted line).

$$Fe^{III} + H_2O_2 \longrightarrow FeOOH \quad (1)$$

$$FeOOH \longrightarrow FeO^{\cdot} + HO^{\cdot} \quad (2)$$

$$HO^{\cdot} + CyH \longrightarrow Cy^{\cdot} \quad (3)$$

$$Cy^{\cdot} + O_2 \longrightarrow CyOO^{\cdot} \quad (4)$$

$$(5)$$

$$Cy^{\cdot} + FeO^{\cdot} \longrightarrow FeOCy \longrightarrow Cyclohexanol \longrightarrow Cyclohexanone \quad (6)$$

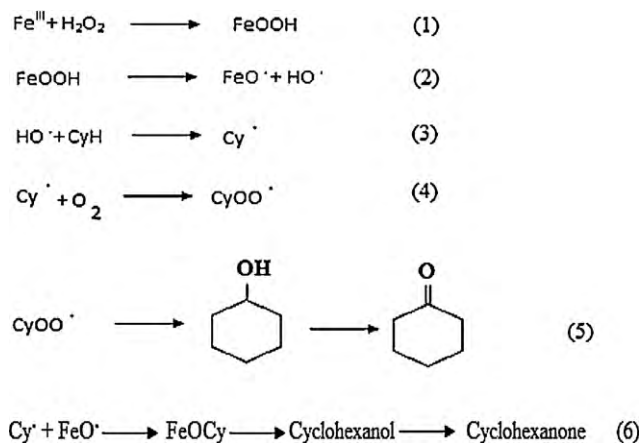**Scheme 3.** Possible mechanistic pathway for cyclohexane oxidation.

3.2. Catalytic oxidation pathway

Cyclohexane oxidation over a variety of Schiff base complex containing different transition metal has been studied in the recent past. Zhao et al. have reported oxidation of cyclohexane with 45.5% conversion using vanadium salen complex supported MCM-41 as catalyst. The reaction was carried out using H_2O_2 as oxidant and acetonitrile as solvent at 60 °C for 12 h [32]. Salavati-Niasari et al. have reported 46.8% conversion using Cu(II) bis(salicylaldehyde) oxaloyldihydrazone encapsulated zeolite [33]. Nevertheless; reports on cyclohexane oxidation over metal complex intercalated LDH are rather scarce. In our experiment we have tested the ability of Fe(III)-Schiff base complex intercalated LDH to catalyze the oxidation of cyclohexane with H_2O_2 as oxidant and acetonitrile as solvent. At early stage of the reaction cyclohexanol predominates but with prolonged reaction time it further oxidizes to cyclohexanone. Our catalyst is selective towards cyclohexanol and cyclohexanone. It does not promote to form any other oxidized product. The immobilized complex showed good catalytic activity under mild conditions.

3.2.1. Proposed mechanism for cyclohexane oxidation

Mechanism involving heterolysis of a peroxide bond to generate high valent oxo-metal intermediate has been proposed for the metal catalyzed oxidation of cyclohexane by hydrogen peroxide [18]. The mechanistic pathway has been depicted in Scheme 3.

Addition of a small amount of CCl$_3$Br (250 μmol) to cyclohexane oxidation reaction gave mainly cyclohexyl bromide demonstrating that reaction proceeds through formation of cyclohexyl free radi-

cal. The cyclohexyl radical formed in the reaction medium might be trapped by O_2 which is formed by consumption of H_2O_2 to form cyclohexyl peroxy radicals (eq^n 4) leading to mixture of alcohol and ketone. Again there is a possibility that FeO$^\bullet$ may react with cyclohexyl radical to produce an iron alkoxy species which leads to the formation of alcohol and ketone. We have also tested our reaction using homogeneous Fe(III)-Schiff base complex as catalyst, but it shows 27% conversion. In case of Fe(III)-Schiff base complex, we are getting less conversion as compare to its heterogeneous counterpart. This may presumably due to the formation of catalytically inactive μ-oxo dimer species by the homogeneous metal complex, as a reason lowers the catalytic activity. But in case of LDH/Fe complex, the active centers are well isolated and separated from each other, which facilitate the oxidation reaction. The self-decomposition of H_2O_2 is obvious in the reaction system; this may hinder the effective utilization of H_2O_2 (Table 1). Several parameters influencing the catalytic properties were investigated and summarized below.

3.2.2. Reaction time

The effect of reaction time on oxidation of cyclohexane was investigated and summarized in Table 2. It was observed that the conversion of cyclohexane gradually increases and reaches a max-

Table 2
Effect of time on conversion.

Time (h)	Conversion (%)	Selectivity (%)	
		Cyclohexanone	Cyclohexanol
2	19.1	48.9	51.1
4	27.4	52.1	47.9
6	32.2	68.4	31.6
8	45.5	72.3	27.7

Reaction temperature 70 °C, amount of catalyst 0.05 g, acetonitrile as solvent.

Table 1
Cyclohexane oxidation under same reaction condition.[a]

Samples	Conversion (%)	Product selectivity[b] (%)			Hydrogen peroxide		
		Cy=O	Cy-OH	BP	SD[c] (%)	Conversion[d] (%)	SE[e] (%)
LDH	–	–	–	–	–	–	–
Fe complex	27	64.7	24.2	11.1	54	68	34
LDH/Fe complex	45.5	72.3	27.7	0	52	64	59

[a] Reaction temperature 70 °C, reaction time 8 h, amount of catalyst 0.05 g, acetonitrile as solvent.
[b] Cy=O (cyclohexanone); Cy-OH (cyclohexanol); BP, byproduct.
[c] Self-decomposition (SD) of H_2O_2 = volume of oxygen released in the reaction.
[d] Conversion of H_2O_2 = consumption of H_2O_2 (including self-decomposition)/initial amount of H_2O_2.
[e] Selectivity (SE) of H_2O_2 = H_2O_2 consumption for product formed/total consumption of H_2O_2.

Table 3
Effect of temperature.

Temperature (°C)	Conversion (%)	Selectivity (%)	
		Cyclohexanone	Cyclohexanol
40	10.7	59.2	40.8
50	20.3	64.7	35.3
60	32.9	68.4	31.6
70	45.5	72.3	27.7
80	34.6	70.9	29.1

Reaction time 8 h, amount of catalyst 0.05 g, acetonitrile as solvent.

Table 4
Catalytic reusability test for LDH/Fe complex.

No. of cycles	Metal content from AAS analysis (wt%)	Conversion (%)
Fresh	0.32	45.5
1	0.31	41.8
2	0.29	40.4
3	0.28	38.7

imum of 45.5% after 8 h. The yield of cyclohexanone increased with the prolonged reaction time, but the yield for cyclohexanol decreases accordingly due to further oxidation of cyclohexanol to cyclohexanone under the reaction conditions [32].

3.2.3. Reaction temperature

The effect of reaction temperature from 40 to 80 °C on oxidation of cyclohexane and product distribution is summarized in Table 3. The conversion of cyclohexane increased to a maximum of 45.5% at 70 °C. At the same time the selectivity of cyclohexanone/cyclohexanol mixture still remained 100%. At higher temperature (80 °C), the conversion decreased to 34.6%. This may be a result of the decomposition of H_2O_2 at high reaction temperature.

3.2.4. Catalytic reusability

It is important to verify the stability of the heterogeneous catalyst since metal leaching from the catalyst could be responsible for the lowering of catalytic activity in successive runs. To address this issue, we have undertaken a series of test by performing repeat reaction cycles under the same reaction conditions as described above. At the end of each reaction cycle, the catalyst was recovered by filtration, washed with acetonitrile and ethanol, dried and reused. Cyclohexane conversion dropped from 45.5 to 41.8% after the first run (Table 4) and remained almost identical after the second run. Further experiments on the stability of the catalyst during cyclohexane oxidation were performed by the hot filtration technique. The catalyst was filtered off at 70 °C after 1 h in order to avoid re-adsorption of leached iron onto the catalyst surface. The reaction still proceeded, but with a substantially lower conversion than in the presence of the catalyst.

4. Conclusions

Zn/Al LDH with Zn:Al molar ratio 3:1 was prepared by co-precipitation method at constant pH. XRD pattern confirms the increase in basal spacing of the resulting complex intercalated LDH from 8.67 Å to 12.43 Å. FT-IR, UV–vis DRS, TGA curves suggests that there is strong interaction between the host layer and intercalated anions. The LDH/Fe complex so formed found to be an efficient catalyst for liquid phase oxidation of cyclohexane (45.5%) using H_2O_2 as oxidant. The reaction is selective towards cyclohexanone (72.3%) and cyclohexanol (27.7%). Recycling and hot filtration results indicate that the catalyst is stable for further oxidation reaction up to three cycles. Generally, we can say the Fe(III)-Schiff base complex can be considered as a good catalyst for cyclohexane oxidation under mild reaction conditions.

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