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Synthesis, characterization and catalytic activity of Cu(II) Schiff base complexes intercalated in layered double hydroxide for the oxidation of styrene

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A heterogeneous copper Schiff base complex intercalated in layered double hydroxide, abbreviated as LDH-[SALABA-Cu(II)] has been synthesized and characterized by various analytical techniques like XRD, EDX, FTIR, SEM, ICP-AES, TGA, BET surface area, XPS etc. Its catalytic activity has been examined for oxidation of styrene using 70% *tert*-butyl hydroperoxide as an oxidant in acetonitrile solvent. The oxidation products have been styrene oxide, benzaldehyde and benzoic acid have been obtained in which styrene oxide is obtained as major oxidation product under optimized conditions. A maximum 81.27% conversion of styrene has been obtained after 5 h of reaction. The catalyst, LDH-[SALABA-Cu(II)] has been recycled ten times in consecutive runs without much loss of catalytic activity. Quenching study has also been performed using p-benzoquinone in order to find out the mode of mechanism.

Keywords: Layered double hydroxides, heterogeneous catalyst, styrene, oxidation, *tert*-butyl hydroperoxide

The process of oxidation is an important chemical reaction as it gives several useful products from different substrates[1,2]. The conversion of styrene to styrene oxide, benzaldehyde and benzoic acid is of great interest for industries because of their wide uses. The benzaldehyde is used in production of pharmaceuticals, agrochemicals, resin additives, perfumes, dyestuffs and flavours; styrene oxide is used in production of cosmetics, epoxy resins, surface coatings, perfumes and bulk chemicals while benzoic acid in its salt form is used as preservative in drugs and foods[3,4] Hydrocarbons are very prone for the oxidation specially olefins just due to presence of unsaturation. The process becomes fast in presence of catalysts containing transition metal Schiff base complexes as these are having various stable oxidation states, suitable for redox reactions[5]. Mostly, first row transition metals are used in preparation of homogeneous as well as heterogeneous Schiff base catalysts[6-10]. Various Schiff bases were used in their homogeneous form in which variety of primary amines as well as aldehydes or ketones have been used like R(−)-1-amino-2-propanol, N-methylethylenediamine, 2,2’-dimethyl-propanediamine, 2-ethanolamine, 1,2-diaminocyclohexane as primary amines and salicylaldehyde, 2-hydroxypropiophenone and o-hydroxyacetophenone as carbonyls[11-14]. Copper in its salt and complex form is versatile agent for several oxidation reactions like epoxidation, sulfoxidation and oxidative coupling reactions[15-17]. The homogeneous complexes give good conversion but the system become less preferable due to some drawbacks like non-reusability, difficult product separation etc and hence concept of heterogeneous catalyst made its place in the community of researchers, for the oxidation of hydrocarbons. There are varieties of supports like silica gel, zeolites, clays and ion exchanger which are useful for the purpose of heterogenization of homogeneous catalyst. The process makes the complex more stable and recyclable[13,18-23]. Zeolite-Y supported copper and vanadium complexes [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y have been synthesized for the oxidation of styrene and cyclohexene to obtain variety of products using H_2O_2 as oxidant[15]. Silica supported metal salen complexes have been used for the evaluation of catalytic activity and stability by testing oxidation reactions in the presence of oxidant[18]. Clay in its natural and commercial form is useful for many reactions like oxidation, addition, cyclization, alkylation etc[20]. Besides alumina, silica, zeolite etc ion exchangers have also been used widely as support. Schiff base complexes supported on crystalline α-zirconium phosphates are also suitable for the oxidation reactions of alkene[24,25].

In comparison to other supports, layered double hydroxides (LDHs) have received much attention in view of their potential usefulness as support. It is a good anion exchanger with the formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+}.(A^{n-}_{x/n}).mH_2O$, where A^{n-} is the interlayer anion of charge n that leads to the electro-neutrality of LDH. The coefficient x is equal to the molar ratio ($M^{III}/M^{II}+M^{III}$), and m is the number of water molecules located in the interlayer region together with the anions[26-28]. Presently layered double hydroxides (LDHs) have received significant attention due to their potential applications as catalysts, drug delivery agent, lubricant and intercalation chemistry[29-34].

In previous studies, we have reported layered material supported recyclable heterogeneous catalysts for the oxidation of cyclohexene, cyclohexane and styrene[35-38]. In the present paper, we are reporting synthesis of copper Schiff base complexes, derived from salicylaldehyde and 4-amino benzoic acid {SALABA-Cu(II)}, which was intercalated in layered double hydroxide. The heterogeneous catalyst is abbreviated as LDH-[SALABA-Cu(II)] and is studied for the oxidation of styrene using TBHP as an oxidant.

Materials and Methods

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3.9H2O$), sodium hydroxide, 4-amino benzoic acid, salicylaldehyde, copper acetate, and styrene were purchased from E. Merck. Purity of styrene has been checked by gas chromatography (G.C.) to ensure the absence of any oxidation product present in it. The 70% TBHP (in water) is purchased from Loba. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 discover diffractometer in the 2θ range of 2-70° using CuKα radiation (λ = 1.5418 Å) at scanning speed 3 sec per step size 0.02°. Scanning electron microscopy (SEM) measurements has been performed using a JEOL JSM 6100 electron microscope, operating at 20 kV. The Fourier transform infrared (FTIR) spectra are recorded on Perkin Elmer model 1750 in KBr. Thermogravimetric analysis (TGA) is conducted on a Shimadzu TGA-50 system in the range 298–1023 K, at heating rate of 10 °C min^{-1}. BET Surface area of the catalysts was measured using Micromeritics accelerated surface area and porosimetry system (ASAP 2020) at liquid nitrogen temperature (77 K). ICP-AES analysis is done by Thermo Electron IRIS INTREPID II XSP DUO with Spectral range165 to >1000 nm by using CID Detector. Analytical gas chromatography was carried out on a Shimadzu Gas Chromatograph GC-14B with dual flame ionization detector (FID) having XE-60 ss column at 393 K and attached with Shimadzu printer. The products were identified by GC-MS (Perkin-Elmer Clasus 500 column; 30 m × 60 mm)

Preparation of catalyst

Preparation of neat [SALABA-Cu(II)] complexes

The Cu(II) complex has been synthesized *insitu* by dissolving 4-amino benzoic acid (10 mmol) into a 50 mL methanolic solution of NaOH (20 mmol) with continuous stirring at room temperature, a solution of Salicylaldehyde (10 mmol) in 50 mL methanol is added into this solution then immediately copper acetate (5 mmol) is added and the mixture is kept under continuous stirring for 4 h at room temperature. After 4 h the greenish precipitate of SALABA-Cu(II) complexes are formed. Now, the precipitates are filtered, washed with petroleum ether and dried in air. The obtained complexes have been characterized by elemental analysis and CHN, FTIR and UV. In SALABA-Cu(II) complexes, the elemental percentage of CHN is following: Anal.(%) calcd. for $C_{28}H_{20}N_2O_6Cu$: C, 61.82; H, 3.68; N, 5.15. Found: C, 61.53; H, 3.59; N, 5.06%. IR (ν, cm^{-1}): 1380 (NO_3^-), 1531 (C=O), 1596 (C=N), 3323 (O-H), 1280 (Cu-N), 507 (Cu-O). λ_{max} / nm (ε_{max} /LM^{-1} cm^{-1}) (methanol) 231(22000), 281 (21000), 355 (12000), 716 (5000).

Preparation of heterogeneous catalysts, LDH-[SALABA-Cu(II)]

The LDH-[SALABA-Cu(II)] catalyst is synthesized in three steps.

First step is synthesis of amino benzoic acid-layered double hydroxide (abbreviated as LDH-[NH_2-C_6H_4COO]), which is done by co-precipitation method as reported in literature[39] after little modifications. Two separate aqueous solutions of metal salts are prepared. First solution consists of (0.10 mol) zinc nitrate hexahydrate {$Zn(NO_3)_2.6H_2O$} and (0.03 mol) aluminium nitrate nonahydrate {$Al(NO_3)_3.9H_2O$}, dissolved in deionised water while second solution is prepared by dissolving 0.15mol

4-amino benzoic acid in an alkaline solution of sodium hydroxide in deionised water. Aforesaid solutions are mixed together slowly with continuous stirring using magnetic stirrer. As the two solutions react together, precipitation gets started. This mixture is digested at 338 K for 66 h. After digestion the mixture is cooled and solid counterpart is separated by simple filtration and washed many times with deionised water followed by methanol to remove unreacted amino benzoic acid if any. Now the obtained product is dried overnight at 333 K. Such obtained material is known to be LDH-[NH_2-C_6H_4COO].

The second step is preparation of LDH-salicylaldimine ligand {LDH-(SALABA)}. LDH-[NH_2-C_6H_4COO] (1 g) is suspended in 50 mL of methanol in a 250 mL round bottom flask, equipped with condenser and it is added with salicylaldehyde (1.6 mmol) and refluxed for 4 h under nitrogen atmosphere at 353 K. Yellow coloured solid is obtained, which is filtered and washed with methanol several times until the supernatant liquid becomes colourless.

The third step is synthesis of heterogeneous catalyst, LDH-[SALABA-Cu(II)], which is done by using ligand LDH-(SALABA) and copper acetate. For the preparation of LDH-[SALABA-Cu(II)], 1 g of ligand LDH-[SALABA], suspended in 50 mL methanol is mixed with 1.4 mmol of copper acetate, dissolved in 50 mL methanol in a 250 mL round bottom flask. The mixture is refluxed under nitrogen atmosphere for another 3 h at 353 K. Greenish coloured solid is filtered and washed with methanol. Then Soxhlet extraction by methanol, acetone, dichloromethane followed by acetonitrile was carried out so as to remove unbounded complex on the surface of support.

General procedure for catalytic oxidation of styrene

The catalytic oxidation of styrene has been carried out using LDH-[SALABA-Cu(II)] in three-necked round bottom flask (100 mL) equipped with a refluxed condenser. In a typical experiment, the flask was loaded with required amount of styrene, TBHP, catalyst and internal standard dodecane (0.1 mL). The mixture was stirred at the desired conditions for 5 h. After completion of the reaction, the contents of the flask was cooled in an ice-bath and the catalyst was filtered out so that to stop further reaction which could take place in the presence of catalyst. Such separated liquid layer was analyzed quantitatively by GC using XE-60 ss column at 90 °C and the obtained products were identified by GC-MS. The GC-MS analysis revealed that the products formed in the reaction were benzaldehyde, styrene oxide, and benzoic acid. The percentage conversion of styrene, selectivity of products[21] and turn over number[11] of the products are calculated as:

Substrate conversion (%) = Substrate converted (moles)/ Substrate used (moles)×100 …(1)

Product selectivity (%) = Product formed (moles)/ Substrate converted (moles)×100 …(2)

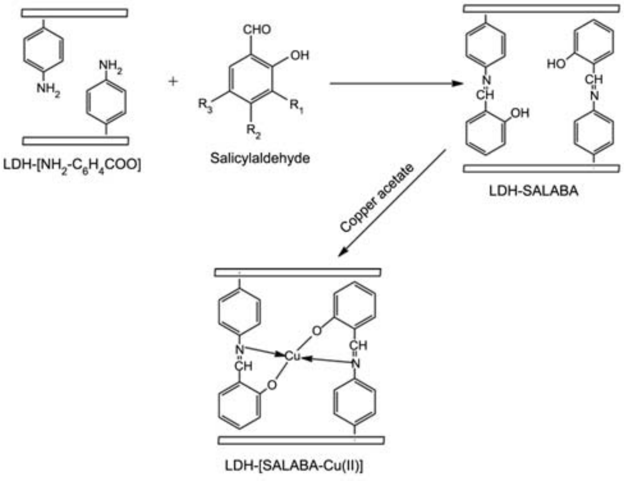
Turn over number = mmol of product/ mmol of catalyst …(3)

Results and Discussion

Characterization of the catalyst

The heterogeneous catalyst, LDH-[SALABA-Cu(II)] has been prepared by the intercalation of Cu-Schiff base complex in LDH-[NH_2-C_6H_4COO]. The preparation of LDH-[SALABA-Cu(II)] is shown in Scheme 1.

Chemical composition and textural properties of support and heterogeneous catalyst are given in Table 1. The ICP-AES analysis shows the percentage of metal present in the catalysts. The elemental composition of the heterogeneous catalyst has been determined by EDX analysis. The EDX measurements results are incorporated in Table 1 and in Supplementary Data, Fig. S1. The presence of zinc, aluminium, carbon, oxygen, nitrogen along with copper metal in LDH-[SALABA-Cu(II)] confirms its formation. The ideal formula of LDH-[SALABA-Cu(II)], based on the elemental content and Zn/Al ratio, is $[Zn_{0.75}Al_{0.25}(OH)_2][\text{SALABA-Cu(II)}]_{0.12}.(H_2O)_2]_{0.12}[NH_2\text{-}C_6H_4COO]_{0.06}\cdot 1.77H_2O$.



Synthesis of heterogeneous catalyst, LDH-[SALABA-Cu(II)]

Scheme 1

Table 1 — Analytical data and textural properties of support and heterogeneous catalyst

Component	*Copper Content (%)	EDX Data (Wt%)						BET Surface Area (m^2g^{-1})	d-spacing (Å)	Particle size (nm)
		Zn	Al	C	O	N	Cu			
LDH-[NH_2-C_6H_5COO]	-	26.39	7.73	32.49	29.12	4.27	-	6.92	15.65	2.1
*LDH-SALABA-Cu(II)[b]	7.19	23.54	7.75	41.92	16.19	3.38	7.22	26.44	22.69	2.5
*LDH-SALABA-Cu(II)[a]	6.53	23.52	7.65	42.81	16.07	3.26	6.69	23.36	21.87	2.8

* a: After catalysis, b: Before catalysis.*ICP-AES analysis

The surface area of heterogeneous catalysts has been determined by BET method. The surface area[40] of support LDH-[NH_2-C_6H_4COO] is found to be 6.92 m^2/g whereas the surface area of LDH-[SALABA-Cu(II)][b] and LDH-[SALABA-Cu(II)][a] 26.44, 23.36 m^2/g respectively (Table 1). The higher surface area of catalyst than support clearly indicates the presence of copper Schiff base complex in the inter layers of LDH-[NH_2-C_6H_4COO]. Additionally, XRD analysis also provides evidence of intercalation of copper Schiff base complexes in the interlayer of LDH-[NH_2-C_6H_4COO].

XRD analysis is useful for obtaining d-spacing with the help of Bragg's equation ($n\lambda = 2d\ Sin\theta$) by using 2θ value. XRD patterns of LDH-[NH_2-C_6H_4COO], LDH-[SALABA-Cu(II)] shows the d-spacing corresponding to the plane (003) (Fig. 1). The characteristic reflections corresponded to (110) plane shows atomic distribution density depending on molar ratio[41] of Zn/Al. The basal d-spacing (15.65 Å) in LDH-[NH_2-C_6H_4COO] is in good agreement with earlier reported data[39]. When this LDH-[NH_2-C_6H_4COO] is converted to ligand by interaction of salicylaldehyde with it, the d-spacing increases to 22.69 Å. Upon incorporation of copper ions, d-spacing becomes 22.69 and 21.87 Å in LDH-[SALABA-Cu(II)][b] and LDH-[SALABA-Cu(II)][a] respectively with gallery height 17.99 and 17.17 after subtraction of thickness of brucite layers (4.7 Å). The increase in gallery height of hydrotalcite indicates successful intercalation of Cu Schiff base complex inside the layers of hydrotalcite. Furthermore, particle size of support and heterogeneous catalysts has been calculated using Debye-Scherrer equation (Table 1).

The thermal decomposition behavior of LDH-[NH_2-C_6H_4COO] and LDH-[SALABA-Cu(II)] was evaluated by TGA analysis (Fig. 2). The mass loss in the TGA curve of LDH-[NH_2-C_6H_4COO] in temperature range 25–250 °C (8.02%) and 250–500 °C are due to the removal of physically adsorbed and intercalated water and degradation of the brucite like layer (28.13%). Whereas the TGA curve of LDH-[SALABA-Cu(II)] shows first mass loss behavior from 25–290 °C due to the removal of physically adsorbed and intercalated water (9.85%). The second stage corresponds to the degradation of the brucite like layer as well as catalyst between 290–650 °C (27.95%).

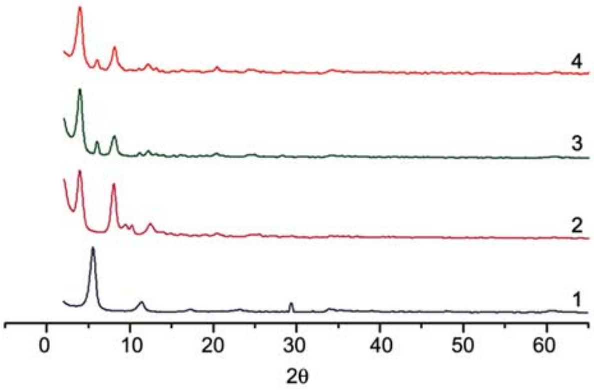


Fig. 1 — XRD pattern (a) LDH-[NH_2-C_6H_4COO], (b) LDH-[SALABA], (c) LDH-[SALABA-Cu(II)], and, (d) Recycled LDH-[SALABA-Cu(II)].

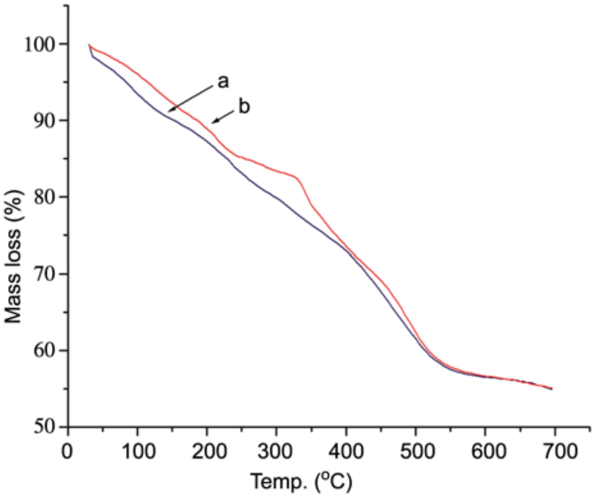


Fig. 2 — TGA curves of (a) LDH-[NH_2-C_6H_4COO] and (b) LDH-[SALABA-Cu(II)].

SEM is useful for examination of morphology of LDH-[NH_2-C_6H_4COO] and LDH-[SALABA-Cu(II)]. The SEM images indicate the presence of several small irregular lamellar crystals, which are compactly agglomerated (Fig. 3). These results indicate that the morphology of the host hydrotalcite-like material is not significantly influenced by the intercalation of the Copper Schiff base complex into the LDH host by partial substitution of benzoate ions.

The FT-IR spectrum of LDH-[NH_2-C_6H_4COO] shows merged absorption band due to stretching mode of OH and NH_2 in the region 3051–3493 cm^{-1} which is ambiguous while absorption band at 1382 cm^{-1}, appears due to the presence of NO_3^- group[42]. The band due to νC=O appears at 1536 cm^{-1}. The M-O (558, 604, and 827 cm^{-1}) and O-M-O (428 cm^{-1}) vibrations are assigned as lattice vibration modes of the LDH sheets, where M denotes zinc and aluminium[43]. It is clear from the Supplementary Data, Fig. S2 that stretching modes at 1608, 1549 and 3233 cm^{-1} are due to C=N, C=O and O-H, present in ligand LDH-[SALABA]. When ligand is coordinated with metal salts and complexation occurs, then the band appearing at 1608 cm^{-1} is shifted in the homogeneous as well as heterogeneous catalyst. Along with the imine group, the presence of stretching peak in range of 412–586 and 488–755 cm^{-1} are attributed to Cu-N and Cu-O in homogeneous and heterogeneous complexes. The strong band in the range of 3118–3331 cm^{-1} attributes[44] to ν(O-H). The presence of bands, approximate in the same regions in of LDH-[NH_2-C_6H_4COO] and LDH-[SALABA-Cu(II)] indicates that intercalation of copper Schiff base complex does not affect the basic structure of LDH-[NH_2-C_6H_4COO].

The XPS Spectra gives very important information regarding the presence of elements in any complex and the oxidation state of metal as well. The Zn, Al, C 1s, N 1s and O 1s appears at 1025.66, 94.43, 289.06, 404.09 and 535.94 eV respectively in LDH-[NH_2-C_6H_4COO], (Fig. 4a). In LDH-[SALABA-Cu(II)] peaks at 1025.66, 96.44, 289.06, 404.09 and 535.94 eV shows the presence of the Zn, Al, C 1s, N 1s and O 1s respectively (Fig. 4b). Except these peaks, the peaks at 939.77 and 947.31 eV are due to Cu $2p_{3/2}$ and Cu $2p_{1/2,}$ which indicaes the presence of copper metal in catalyst in +2 oxidation state[45].

Catalytic oxidation of styrene

The oxidation of styrene is investigated under similar reaction conditions by using heterogeneous

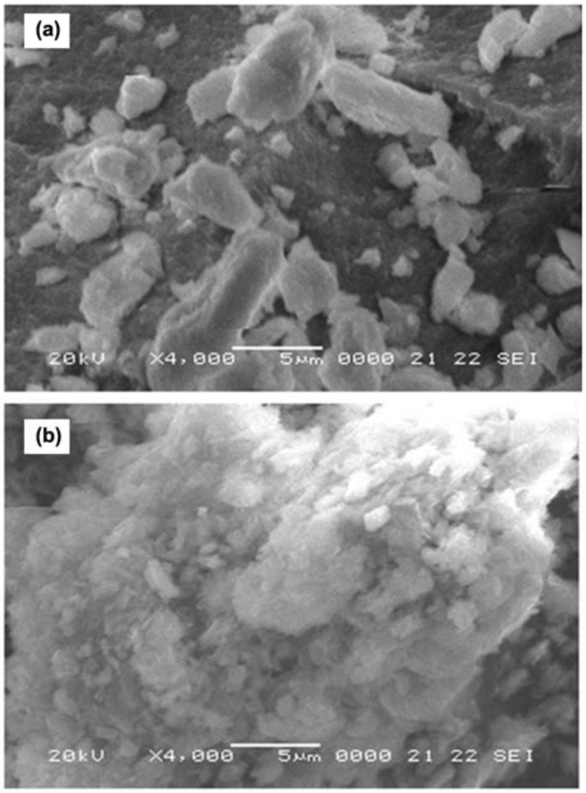


Fig. 3 — SEM images of (a) LDH-[NH_2-C_6H_4COO] and (b) LDH-[SALABA-Cu(II)].

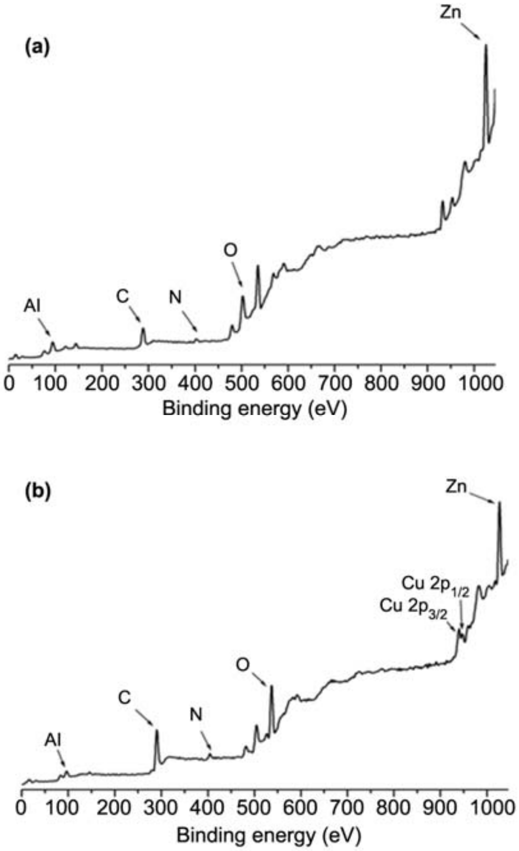


Fig. 4 — XPS Spectra (a) LDH-[NH_2-C_6H_4COO] and (b) LDH-[SALABA-Cu(II)].

catalyst, LDH-[SALABA-Cu(II)] and homogeneous catalyst, [SALABA-Cu(II)] and copper acetate monohydrate, $Cu(OAc)_2.H_2O$ using *tert*-butyl hydroperoxide, as an oxidant. The results are included in Table 2. The support i.e., LDH-[NH_2-C_6H_4COO] has also been tested under similar conditions but it gave no conversion which proves it to be catalytically inactive. Along with it some other blank reactions were also performed. The first reaction includes reaction consisting of substrate, oxidant and solvent i.e., without catalyst and obtained result indicates trace amount of products. The same reaction is performed using substrate, catalyst and solvent in the lack of oxidant but this reaction also gave no conversion. The results of blank reactions indicate that the oxidation reaction can only be carried out successfully in the presence of all the components like catalyst, substrate, oxidant and solvent. The heterogeneous as well as homogeneous catalysts are found to be active for the oxidation of styrene. Upon oxidation benzaldehyde, styrene oxide, and benzoic acid are obtained. The consumption of TBHP is determined iodometrically after each catalytic reaction. The catalytic oxidation of styrene, catalyzed by LDH-[SALABA-Cu(II)]/TBHP is explained in Scheme 2.

Optimization study

For deriving optimum conditions to obtain maximum conversion of styrene using LDH-[SALABA-Cu(II)], various parameters like effects of various oxidants, effects of various solvents, molar ratio of styrene to TBHP, concentration of catalyst and reaction temperature have been studied in detail.

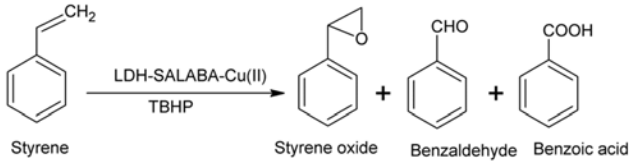
Variety of oxidants viz. molecular oxygen, H_2O_2 and TBHP have been tested but only TBHP is able to convert styrene into products while other two are very less active towards oxidation reaction of styrene (Table 2). Hence TBHP is being used for further oxidation.

Various solvents like polar aprotic, non-polar and polar protic solvents were studied in order to obtain maximum conversion of styrene. For this purpose 50 mg LDH-[SALABA-Cu(II)] , 353 K temperature, 1:1 molar ratio of substrate to oxidant has been observed by varying different solvents (7 mL). When acetonitrile is used as a solvent by taking above mentioned condition, then 55.35% conversion is obtained. Similarly when benzene, methanol and dichloromethane have been used as a solvent then 42.67%, 14.67% and 17.42% conversion of styrene are obtained respectively (Table 2). The results indicate that polar aprotic solvent like acetonitrile favours highest conversion followed by non-polar solvents like benzene, dichloromethane while polar protic solvent like methanol causes decrease in conversion. The decreasing trend of conversion is as follows:

Acetonitrile > benzene > dichloromethane > methanol

Thus the maximum conversion is obtained in case of acetonitrile and hence it has been taken for further observations.

The effect of TBHP concentration on the oxidation of styrene has been studied by considering three



Oxidation of styrene
Scheme 2

Table 2 — Effect of support, various oxidants, and solvents on the catalytic activity of LDH-SALABA-Cu(II)/TBHP on the oxidation of styrene

Entry	System	Conversion of Styrene (%)	Selectivity of Products (%)		
			Benzaldehyde	Styrene oxide	Benzoic acid
1	$Cu(OAc)_2.H_2O$/ Acetonitrile	5.29	17.53	78.86	3.61
2	LDH-[NH_2-C_6H_4COO]	-	-	-	-
3	Without catalyst	3.29	15.49	76.58	21.93
4	Without oxidant	-	-	-	-
5	H_2O_2/ Acetonitrile	11.91	26.49	45.34	28.17
6	O_2/ Acetonitrile	7.95	5.19	78.94	15.87
7	TBHP/ Acetonitrile	55.35	5.56	76.51	17.93
8	TBHP/ Benzene	42.67	3.36	78.57	18.07
9	TBHP/ Dichloromethane	17.42	18.75	64.58	16.67
10	TBHP/ Methanol	14.67	8.96	65.67	25.37

different molar ratios (styrene to TBHP) like 1:1, 1:2 and1:3 (Table 3). All the molar ratios have been tested taking 50 mg LDH-[SALABA-Cu(II)], 353 K temperature and 7 mL acetonitrile as a solvent with varying molar ratios. When 1:1 is taken as molar ratio then 55.35% conversion with 76.51% selectivity of styrene oxide is obtained. An increase is observed when molar ratio increases to 1:2 where conversion of styrene is found to be 59.15% with 77.46% selectivity of styrene oxide. Similarly when molar ratio is increased to 1:3 then conversion increases slightly and reaches to 60.29% with 25.33% selectivity of styrene oxide. However with increase in molar ratio conversion increases linearly but still 1:2 is considered as optimum molar ratio in spite of 1:3 because of two reasons. Firstly conversion increases slightly (only 1.14%) moving towards 1:3 from 1:2, secondly great loss of selectivity of styrene oxide occurs with increase in selectivity of undesired products at 1:3 molar ratio. That is why 1:2 has been chosen as an optimum molar ratio for further observations.

The concentration of catalyst also plays very important role in any catalytic reaction. It basically provides surface to substrate as well as oxidant molecule so that they may come close together and react with each other rapidly. For it, three different concentrations viz. 50 mg, 75 mg and 100 mg are taken under consideration at 1:2 molar ratio of substrate to oxidant, 353 K temperature and 7 mL acetonitrile as a solvent (Table 3). When concentration of catalyst is taken 50 mg then 59.15% conversion is obtained with 77.46% selectivity of styrene oxide. When the concentration of catalyst is increased to 75 mg then conversion of styrene reaches to 81.27% with 59.31% selectivity of styrene oxide. Conversion decreases slightly to 78.59% at 100 mg of catalyst concentration where selectivity of styrene oxide is 57.29%. From the above data, it is clear that upon increasing concentration from 50 mg to 75 mg conversion increases by 22.12% while upon increasing concentration from 75 mg to 100 mg conversion increases by 2.68%. The decrease in conversion upon increasing catalyst amount may be attributed to lack of close proximity which is required, between substrate and oxidant to interact. It is due to availability of excess amount of catalyst[7]. Hence, 75 mg concentration is taken as optimum catalyst concentration for further observations.

Temperature is an important parameter for catalytic reaction. Here in our reaction system we observed three different temperatures viz. 343, 353 and 363 K at 1:2 oxidant ratio, 75 mg catalyst concentration and 7 mL acetonitrile as a solvent (Table 3). When the temperature is 343 K then 70.50% conversion with 45.92% selectivity of styrene oxide of styrene is obtained but it reaches to 81.27% with 59.31% selectivity of styrene oxide, when temperature is raised by 10 K i.e., at 353 K. It means 10.77% increase occurs by elevation of 10 K temperature. Now if temperature of system is increased to 363 K then it is found that no major increase occurs in conversion and only 82.59% conversion of styrene is obtained with 32.24% selectivity of styrene oxide. It is found that higher temperature favours formation of various side products due to which negative impact occurs on selectivity of the major product. Keeping all these factors under consideration, 353 K is taken as optimum temperature.

Therefore optimum conditions for obtaining maximum conversion of styrene into products are 75 mg catalyst concentration {LDH-[SALABA-Cu(II)]}, 1:2 molar ratio of substrate to oxidant, 353 K temperature and acetonitrile as solvent, in

Table 3 — Effect of various parameters on the oxidation of styrene catalyzed by LDH-[SALABA-Cu(II)]/TBHP

Styrene: TBHP (molar ratio)	Catalysts Amount (mg)	Temperature (K)	Conversion (%)	*Product Selectivity (%)			TON
				Ben.	S.O.	B.A.	
1:1	50	353	55.35	5.56	76.51	17.98	910
1:2	50	353	59.15	4.04	77.46	18.50	947
1:3	50	353	60.29	10.19	25.33	64.49	962
1:2	75	353	81.27	22.08	59.31	18.61	864
1:2	100	353	78.59	23.49	57.29	19.21	636
1:2	75	343	70.50	9.02	45.92	45.07	764
1:2	75	363	82.59	21.02	32.24	46.73	881

*Ben. = Benzaldehyde, S. O. = Styrene Oxide, B.A. = Benzoic Acid which 81.27% conversion of styrene is obtained. In the similar reaction conditions, when homogeneous catalyst of copper [SALABA-Cu(II)] is tested, then 66.65% conversion of styrene is obtained. The huge difference indicates greater efficiency of heterogeneous catalyst over homogeneous ones. The styrene oxide is obtained as the major product in both cases. Comparison of our work done with other researchers is shown in Supplementary Data, Table S5.

Recyclability

The aim of synthesizing heterogeneous catalyst is its reuse in several consecutive cycles. To check its recycling property the same catalyst is used for the ten times under similar reaction conditions after performing washing with methanol, acetone and acetonitrile and drying at 333 K (Fig. 5). The fresh catalyst gives 81.27% conversion, while in first run, conversion increases and reaches to 85.45%. In second run, conversion again reaches almost equal to fresh catalyst i.e., 80.95%. After second run, conversion gradually drops to 77.67, 75.84, 73.11, 71.22, 71.02, 70.95, 70.22 and 69.73% in third, fourth, fifth, sixth, seventh, eighth, ninth and tenth cycles respectively. The observed decrease in conversion from first to tenth cycle is 15.72%. Therefore whole experiment indicates that catalyst is stable and recyclable enough up to ten cycles efficiently.

Mechanism of the reaction

To find out the mechanism of reaction using TBHP, Quenching experiment has been performed. Generally TBHP provides free radicals for the reaction and motto of this experiment is to capture the aforesaid free radicals by quenching agent (p- Benzoquinone) so that activity gets stopped and no further conversion should be obtained.

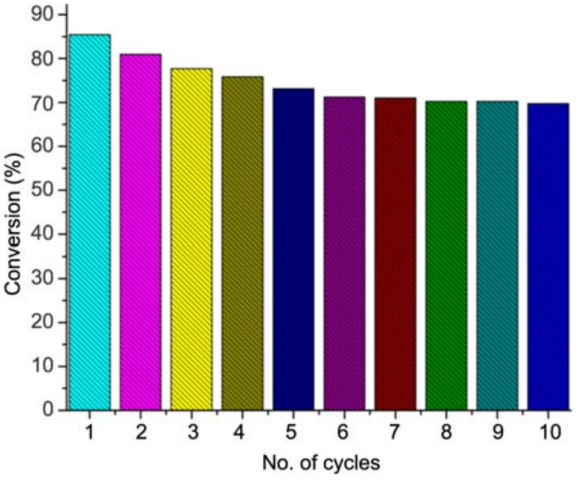
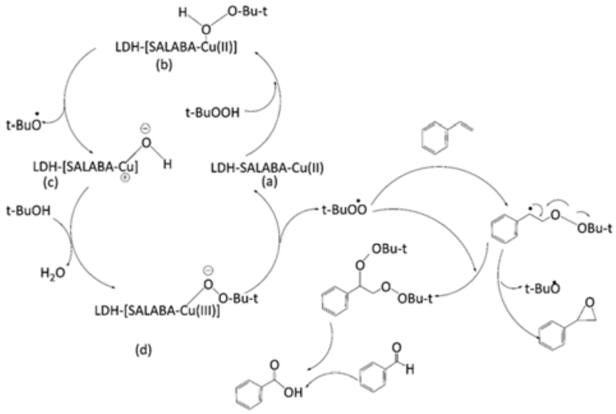


Fig. 5 — Recycling of Catalyst.

For it two parallel reactions have been studied with respect to time from initial (0 h) to 5 h. In the first reaction no quenching agent is added while in the second experiment p-Benzoquinone equimolar to TBHP was added after 3 h of reaction. It is evident from Supplementary Data, Fig. S3 that there is no major change in conversion till 3 h for both reaction but after 3 h, first reaction continues to occur to the end while in second reaction conversion become stagnant and no further increase in conversion is observed after next 3 h. This observation proves that due to the presence of quenching agent, TBHP is not able to provide free radicals due to trapping of free radicals hence no further conversion is observed and also in the GC graph the peak of TBHP disappears completely at the end of the reaction. It is in strong agreement with free radical mechanism.

In the first step, adsorption of oxidant molecules (TBHP) on the surface of metal occurs, which results in coordination between metal centre and TBHP. Second step comprises of generation of *tert*-Butoxy radical species and copper hydroperoxide species. In the third step, another molecule of oxidant reacts with copper hydroperoxide species, leading to elimination of water molecule and formation of copper hydroperoxo species. Finally Cu-O bond cleavage of copper hydroperoxo species takes place which generates *tert*-Butylperoxy radicals and the catalytic cycle restarts. The double bond of styrene is now attacked by *tert*-Butylperoxy radical, for the formation of benzyl radical derivative. This step leads to the formation of styrene oxide and *t*-BuOH as a result of migration of oxygen atom.

The another pathway which could proceed to form benzaldehyde, is the attack of other molecule of *tert*-Butylperoxy radical on benzyl radical which causes oxidative C-C bond cleavage and generation of second oxidation product benzaldehyde. Upon further oxidation, benzaldehyde converts to benzoic acid, which is the third oxidation product. As the results indicate, most favourable pathway is the pathway which undergoes formation of styrene oxide. The whole steps are illustrated in Scheme 3. Similar mechanism is reported[46,47].



The probable mechanism for oxidation of styrene with TBHP catalyzed by the LDH-[SALABA-Cu(II) catalyst.

Scheme 3

Conclusions

LDH-[NH_2-C_6H_4COO] intercalated copper Schiff base complex, LDH-[SALABA-Cu(II)], has been synthesized using salicylaldehyde by intercalation method and characterised by XRD, EDX, FTIR, ICP-AES, SEM, TGA-DTA, BET surface area, XPS etc. Its catalytic efficiency has been studied for oxidation of styrene. Under optimised condition, 81.27% conversion of styrene with 59.31% selectivity of styrene oxide is obtained using catalyst LDH-[SALABA-Cu(II)]. Among three products viz. Styrene oxide, benzaldehyde and benzoic acid, the major product is styrene oxide. The formed catalyst is recycled ten times without too much loss in catalytic activity and hence proving it to be fantastic catalyst in the sense of stability, activity and reusability. The mechanism of the reaction is proved by Quenching experiment, which indicates that TBHP assisted catalytic oxidation of styrene proceeds via free radical mechanism.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(07)753-762_SupplData.pdf.

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