SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF TUNGSTOCOBALTATE-PILLARED ZnAl-LAYERED DOUBLE HYDROXIDE

Bhabani S. Mohanta[a], Rita Das[b]* and Nigamananda Das[c]

Tungstocobalate, $(Co^{III}W_{12}O_{40})^{5-}$, intercalated ZnAl-layered double hydroxide (ZnAl-CoW$_{12}$) was prepared via rehydration of calcined ZnAl-LDH under nitrogen atmosphere. Characterization by chemical analysis together with powder XRD, FT-IR, TG-DTA and UV-VIS DRS provided evidence of intercalation of $Co^{III}W_{12}O_{40}{}^{5-}$ (58 wt. %) in the interlayer of LDH. The catalytic activity of ZnAl-CoW$_{12}$ was evaluated for hydrogen peroxide mediated decolourisarion of methyl orange and oxidation of benzaldehyde to benzoic acid under varying reaction conditions. ZnAl-CoW$_{12}$ was found effective for both the reactions and stable under the experimental conditions for repetitive use without any noticeable decrease in activity.

* Corresponding Authors
    Phone: +91-9437380056
    E-Mail: dasrita66@rediffmail.com
[a]   Department of Chemistry, North Orissa University, Baripada 757 001, Odisha, India
[b] Department of Chemistry, Rama Devi Women's University, Bhubaneswar 751 022, Odisha, India
 [c] Department of Chemistry, Utkal University, Bhubaneswar 751 004, Odisha, India

Introduction

Polyoxometallates (POMs) constitute a potentially important class of inorganic materials because of their unique properties like structural stability and catalytic efficiency for various organic transformations in homo- and heterogeneous media.[1-3] POMs are known to activate H_2O_2 and subsequently oxidize several organic molecules.[1-8] The oxidizing ability can be systematically controlled by changing the constituent atoms of polyanion structure.[4,8] However, their low surface area and thermal stability in addition to high solubility in aqueous medium limit their utility in many catalytic applications.[9,10] In order to avoid the loss of POMs in reaction medium and increase the surface area for widening their practical applications, POMs are often supported on different solid supports like silica, alumina, resin, clays, zeolites and molecular sieves.[9-15]

Layered double hydroxides (LDHs) is another important class of inorganic layered compounds offering support for hosting a variety of catalytically active anionic species in the interlayer space of metal hydroxide layers.[16] Among them, the POMs are found to be a potentially interesting class of guests for LDHs to develop oxidation catalysts or catalyst precursors for several reactions of chemical and environmental importance.[16-18] A variety of structurally different iso- and heteropolyoxometallates with varying metal have been intercalated in the interlayer of LDHs and their catalytic properties have been studied by several workers.[12,19-24]

The present work pertains to intercalation of a catalytically active POM having strong oxidizing ability of Co^{III} ion, $[CoW_{12}O_{40}]^{5-}$ (CoW_{12}),[14,26] in the interlayer of

ZnAl-layered double hydroxide (ZnAl-LDH), characterization of resulted intercalated sample by various physicochemical methods and evaluation of its catalytic activity for oxidative decolourisation methyl orange (MO) and oxidation benzaldehyde to benzoic acid as the model reactions.

Experimental

Synthesis of materials

ZnAl-LDH (molar ratio of Zn/Al = 3) was prepared by coprecipitation of mixed aqueous solutions of $Zn(NO_3)_2.7H_2O$ and $Al(NO_3)_3.9H_2O$ at ambient temperature under low supersaturating conditions (pH ~ 10).[26] The synthesized sample was calcined at 450 °C for 5 h in air to yield ZnAl-mixed oxide, ZnAl(O). The potassium salt of tunstocobaltate, $K_5[Co^{III}W_{12}O_{40}].20H_2O$, was synthesized following the reported method[25,27] and its purity was checked by spectral analysis.

(CoW_{12}) ion was intercalated in the interlayer LDH through rehydration of calcined LDH in presence desired amount of aqueous solution of $K_5[Co^{III}W_{12}O_{40}].20H_2O$. In typical lot a weighed amount of ZnAl(O) was dispersed in 50 mL of aqueous solution of $K_5[Co^{III}W_{12}O_{40}]$ (0.52 g) and the pH was adjusted to *ca.* 6.5 with dilute HNO_3 solution. The mixture was then stirred under N_2 atmosphere for ~ 4 h. By this time the initial green colour of the solution was changed to colourless indicating almost complete intercalation of tunstocobaltate ion in the LDH interlayer. The resulting solid was separated by centrifugation, washed several times with water and finally with ethanol. The isolated solid was dried at 60°C for 8 h in vacuum. The CoW$_{12}$ intercalated sample was denoted as ZnAl-CoW$_{12}$.

Characterizations

The Zn, Al, Co and W contents in the samples were determined by ICP (Varian Liberty series2). Carbon and nitrogen was analysed by Euro EA Vector elemental

analyser. Powder X-ray diffraction patterns were recorded in a Rigaku (Miniflex II) X-ray diffractometer at a scanning speed of 2°(2θ)/min using Ni filtered CoK$_\alpha$ (30 kV, 15 mA) radiation source. Thermogravimetric measurements in argon atmosphere were performed on a Shimadzu DTG 60 Thermal analyser at a heating rate of 10 °C min^{-1}. FT-IR spectra in KBr phase were recorded on a Shimadzu IR Affinity-1 spectrophotometer averaging 45 scans with a nominal resolution of 4 cm^{-1} to improve signal to noise ratio. The UV-Visible diffuse reflectance spectra were recorded on a Varian UV-Visible spectrophotometer using BaSO$_4$ white standard.

Catalytic activity

The catalytic activity of ZnAl-CoW$_{12}$ was evaluated for oxidative decolourisation of a methyl orange and oxidation of benzaldehyde. Stock solution (500 µM) of methyl orange was prepared by dissolving accurately weighed solid methyl orange (Mecrk, GR) in deionized distilled water and was diluted to desired concentration as and when required. H$_2$O$_2$ (30 % w/v, Merck) and benzaldehyde (Merck, GR) was used as received.

For decolourisation of study, 50 mL of MO at desired concentration along with appropriate amounts of H$_2$O$_2$ and ZnAl-CoW$_{12}$ in a 100 mL conical flask were mechanically shaken in thermostated water bath shaker at 30±0.2 ºC. The initial pH of the reaction mixture was adjusted to 6.0±0.2 by addition of 0.1 M NaOH/HCl solution. At regular intervals, the reaction mixture was withdrawn, centrifuged and measured the absorbance at 464 nm (ε = 2.68×10^4 M^{-1} cm^{-1}) to evaluate the concentration of residual MO. In aqueous solution, MO is almost completely dimerised above 2×10^{-4} M and undergoes further aggregation at millimolar and higher concentrations[29]. Hence, the concentration of MO was kept < 1×10^{-4} M where the Beer–Lambert law is obeyed. All the experiments were carried at pH above the pK$_a$ value of MO (~3.4) in order to avoid any further colour change due to pH variation. The reaction parameters such as time of reaction, catalyst amount and initial concentrations of MO and H$_2$O$_2$ were varied to optimize the parameters.

The oxidation of benzaldehyde was carried out by a similar procedure adopted in a previous study.[14] The reaction mixture containing ZnAl-CoW$_{12}$, benzaldehyde and 30 wt. % H$_2$O$_2$ in a 100 mL flask was heated under stirring condition to initiate the reaction. The reaction time, temperature and amounts of H$_2$O$_2$ and catalyst were varied to optimize the reaction parameters. The formation of benzoic acid is evident from its isolation by similar method described earlier[14] and characterized by FT-IR spectral analysis and melting point measurement. The yield of benzoic acid was calculated from the weight of the final white crystals.

Results and Discussion

Characterizations of ZnAl-CoW$_{12}$

The addition of ZnAl(O) to the green solution of K$_5$[Co^{III}W$_{12}$O$_{40}$].20H$_2$O followed by stirring under N$_2$ atmosphere for 4 h results almost colourless solution

indicating complete intercalation of CoW$_{12}$ in the interlayer of regenerated ZnAl-LDH to yield ZnAl-CoW$_{12}$. The molecular formulae of ZnAl-LDH (carbonate form) and CoW$_{12}$ intercalated LDH (ZnAl-CoW$_{12}$), derived from the chemical analyses, are tentatively represented as [Zn$_{0.74}$Al$_{0.26}$(OH)$_2$](CO$_3$)$_{0.146}$ and [Zn$_{0.73}$Al$_{0.27}$(OH)$_2$] (CoW$_{12}$O$_{40}$)$_{0.045}$(CO$_3$)$_{0.012}$, respectively indicating all the residual positive charge of brucite like layer is not compensated by CoW$_{12}$ ion and about 16.6% of total positive charge is balanced by CO$_3$$^{2-}$/OH$^-$ ions. The wt. % of CoW$_{12}$ in ZnAl-CoW$_{12}$ is ~ 56.2 which is ~ 12% lower than that reported (68.7 wt.%) in the case of corresponding MgAl-CoW$_{12}$ sample.[14] This is primarily due to higher residual positive charge in brucite like layer of MgAl-LDH (Mg/Al = 2) sample, used for intercalation, than ZnAl-LDH (Zn/Al ≈ 3).
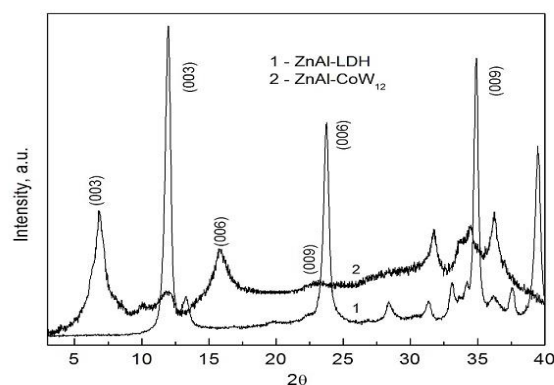

Figure 1. Powder XRD patterns of ZnAl-LDH and ZnAl-CoW$_{12}$.

The powder XRD patterns of ZnAl-CoW$_{12}$ along with ZnAl-LDH are presented in figure 1. The appearance of some new peaks in ZnAl-CoW$_{12}$ and shifting of reflections (003, 006, 009) to lower 2θ values indicate the intercalation of CoW$_{12}$ in the interlayer. The basal spacing, derived from 2θ values, is increased from 7.38 Å to 12.96 Å. Assuming the hydroxide layer thickness of ZnAl-LDH to be 4.8 Å and size of the Keggin ion 10.2 Å, as estimated from crystallographic data for a Keggin ion salt,[14] this increase of basal spacing is quite reasonable. A decrease of crystallinity of ZnAl-CoW$_{12}$ is also evident from its broadened low intensity diffraction peaks.
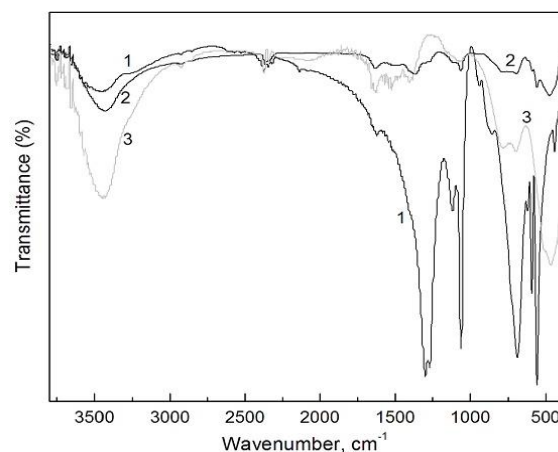

Figure 2. FT-IR spectra of calcined ZnAl-LDH (1), CoW$_{12}$ only (2) and ZnAl-CoW$_{12}$ (3).

The IR spectra of ZnAl-CoW$_{12}$ along with K$_5$[Co^{III}W$_{12}$O$_{40}$] and Zn(Al)O are presented in figure 2. The Keggin-type structure of [CoW$_{12}$O$_{40}$]$^{5-}$ anion consists of one centrally located CoO$_4$ which is caged by 12 octahedral WO$_6$ units linked to one another by the neighbouring oxygen atoms. In general, the asymmetric stretching of the different kinds of W–O bonds is observed in the following spectral regions: W–O$_d$ bonds (1000–900 cm^{-1}), W–O$_b$–W bridges (800–900 cm^{-1}), W–O$_c$–W bridges (700–800 cm^{-1}). The K$_5$[Co^{III}W$_{12}$O$_{40}$]. 20H$_2$O displayed four characteristic bands at 955, 883, 698 and 445 cm^{-1} attributing to v_{as}(W–O$_d$); v_{as}(W–O$_b$–W), v_{as}(W–O$_c$–W), v_{as}(Co–O$_a$) or δ(O–Co–O)[19,30] and are very much similar to those reported previously.[14,15] The bands at 3520 and 1640 cm^{-1} are attributed to the stretching and bending vibrations of O–H and H–O–H bonds. The band positions, although of lower intensities, in the spectra of ZnAl-CoW$_{12}$ are similar to that of K$_5$[Co^{III}W$_{12}$O$_{40}$] providing further evidence of intercalation of [CoW$_{12}$O$_{40}$]$^{5-}$ ions in the interlayer of ZnAl-LDH. After the exchange, the bands due to W–O and Co–O stretching modes are still recorded (938, 885 752 and 440 cm^{-1}), together with other band at 648 cm^{-1} due to the transitional modes of the LDH.
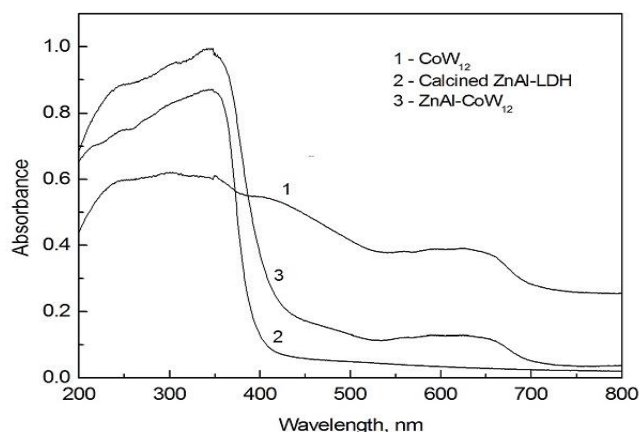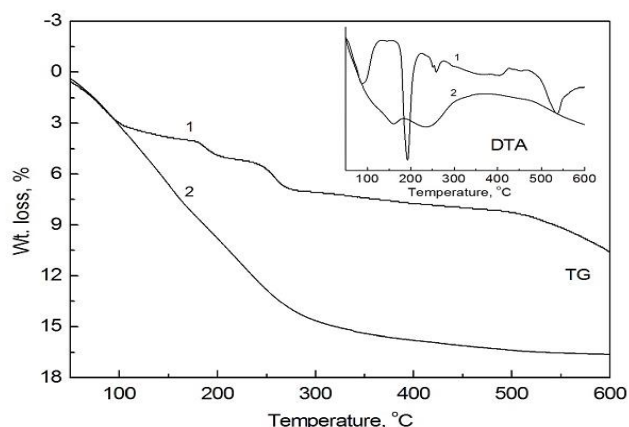

Figure 3. UV-Vis DRS ZnAl-LDH (calcined), ZnAl-CoW$_{12}$ and CoW$_{12}$.

Figure 4. TG and DTA curves of CoW$_{12}$ (1) and ZnAl-CoW$_{12}$ (2) at heating rate 10°C under N$_2$ atmosphere.

More evidence in favour of intercalation of CoW$_{12}$ in the interlayer of LDH is obtained from UV-Vis DRS (Figure 3). The characteristics peaks of CoW$_{12}$ and ZnAl-LDH are also appeared in the case of ZnAl-CoW$_{12}$ indicating the intercalation of CoW$_{12}$ in the interlayer of ZnAl-LDH. The

TG-DTA curves of CoW$_{12}$ and uncalcined ZnAl-CoW$_{12}$ are presented in figure 4. It is seen that ZnAl-CoW$_{12}$ exhibits a continuous weight loss up to 600 °C with two distinct endothermic peaks centered at ~ 160 and 245 °C in the DTA profile. A hump like endothermic peak observed at ~ 120 °C is presumably due to the loss of surface-adsorbed water. The peaks at 160 and 245 °C are attributed to the removal of interlayer water followed by collapse of the layered structure.[14] The weight loss beyond 300 °C is resulted from both the dehydroxylation of ZnAl–LDH layers and the decomposition of CoW$_{12}$ to expel the produced water molecules. The neat complex also exhibits multi stage weight losses with two major endothermic peaks at 90 and 190 ºC.

Catalytic activity of ZnAl-CoW$_{12}$

Oxidative decolourisation of methyl orange (MO)

Preliminary observation indicates practically no change in the absorbance of MO over a period of 3 h in presence of H$_2$O$_2$ (0.05 M) indicating there is no decolourisation of MO by H$_2$O$_2$ alone. As MO exists in anionic form at pH > 4.0, decolourisation due to ion exchange or adsorption of a small amount of MO in the interlayer or surface of ZnAl-CoW$_{12}$, respectively, cannot be ruled out. A typical experiment, with ZnAl-CoW$_{12}$ (0.5 g l^{-1}) and MO (35 μM) and without addition of H$_2$O$_{2,}$ shows (Figure 5, inset) a decrease in absorbance over the entire range of spectrum. The amount of MO decolourised due to ion exchange/adsorption on ZnAl-CoW$_{12}$, estimated using the absorbance values of MO at 275 and 464 nm, is found to be ~ 14 %. In presence of both H$_2$O$_2$ and ZnAl-CoW$_{12}$, the MO peak at 275 nm is not observed (Figure 5) due to high absorbance of H$_2$O$_2$ at < 300 nm. However, the absorbance of MO at 464 nm is progressively decreased with time and reached to almost zero in ~ 8 h. Interestingly the MO peak at 275 nm is reappeared when the concentration of H$_2$O$_2$ is decreased with the progress of reaction.
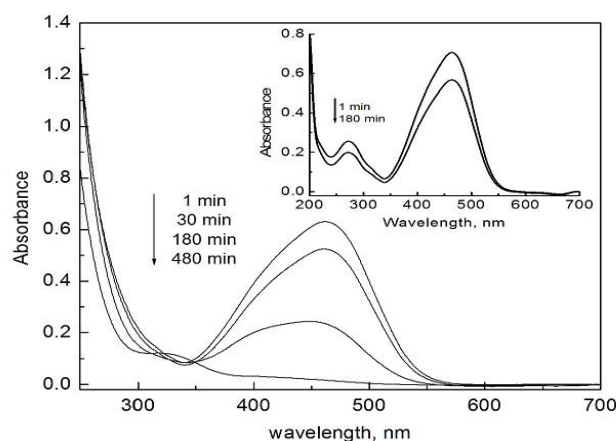

Figure 5. Successive spectral scan of MO (35 μM) with time in presence of ZnAl-CoW$_{12}$ (0.5 g/l) and H$_2$O$_2$ (0.05 M). (Inset) in presence of ZnAl-CoW$_{12}$ (0.5 g/l) only.

As more than 80 % of MO is decolourised within 300 min of reaction, all further decolourisation experiments for determination rate constant and optimization of other parameters were carried out keeping the time of reaction

time fixed at 300 min. The time course percentage of MO decolourised in the presence and absence of H_2O_2 is presented in figure 6. It is seen that the decolourisation of MO is strongly catalysed in presence of both H_2O_2 and catalytic amount of ZnAl-CoW$_{12}$ and more than 80 % MO (35 μM) is decolourised against 14 % decolourisation in the absence of H_2O_2. The decolourisation data up to 300 min are subjected to non-linear least square fitting (eqn. 1).

$$C_t = (C_0 - C_\infty)\, e^{(-kt)} + C_\infty \qquad (1)$$

where C_0, C_t and C_∞ are the concentrations of MO at the beginning, time 't' and the end, respectively and k is the rate constant. The first-order rate constants, derived from least square fittings ($R^2 = 0.99$), are found to be 0.357 ± 0.070 and 0.433 ± 0.051 h^{-1} for 35 and 60 μM MO concentrations, respectively under identical conditions.
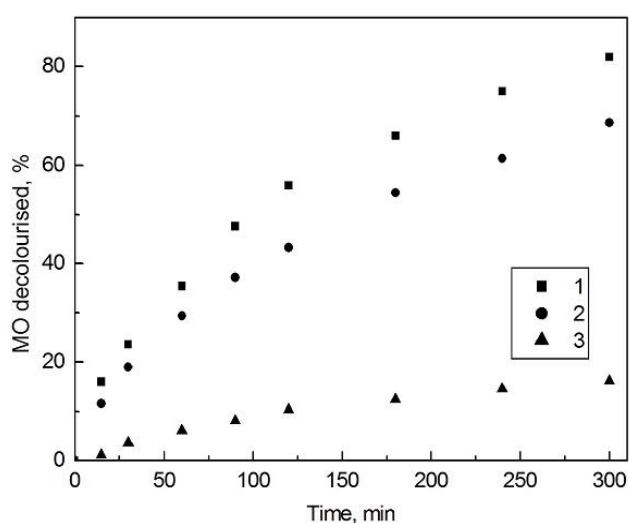

Figure 6. Time course of MO decolourisation in presence of ZnAl-CoW$_{12}$ (0.5 g/l) and $[H_2O_2]$ = 0.02 M at varying MO concentrations: (1) 35 μM, (2) 60 μM and MO decolourisation (35 μM) by ZnAl-CoW$_{12}$ (0.5 g/l) without H_2O_2.

Table 1. Effect of catalyst amount and initial dye concentration on decolourisation of MO.

$[H_2O_2]$, M	ZnAl-CoW$_{12}$, g L^{-1}	MO decolourization, %
0.02	0.20	34.5
0.02	0.50	66.3
0.02	1.00	88.0
0.02	1.50	98.4
0.05	0.50	76.5
0.10	0.50	87.2
0.015	0.50	90.9
0.20	0.50	93.4

[MO] 35 μM, reaction time 300 min, temperature 30±0.2 ºC.

The effect of initial H_2O_2 concentration (0.02 to 0.20 M), keeping the dye and catalyst amounts fixed, is presented in Table 1. It is seen that the percentage of decolourisation increases non-linearly with increase of initial concentration of H_2O_2. The decrease of oxidation activity of H_2O_2 at higher concentration is most likely due to increase of catalysed H_2O_2 decomposition at higher concentration. The

effect of catalyst amount on overall MO decolourisation, keeping all other parameters fixed, is also presented in Table 1. The decolourisation is progressively increased due to availability of more active component for catalysis and sites for adsorption/ion exchange. In order to see the efficiency of ZnAl-CoW$_{12}$ for repetitive use, the reactant solution was charged with desired amount of MO and H_2O_2 after every 5 h to maintain the same initial MO (35 μM) and H_2O_2 (0.05 M) concentrations. In the first round, 76.1 % of 35 μM MO is decolourised in 5 h at initial pH ~ 6.0 and ZnAl-CoW$_{12}$ dose of 0.50 g L^{-1}. In the second round with a fresh load of MO and H_2O_2, to maintain the same initial concentrations, 64.1% of MO is decolourised. In third and fourth cycles, the percentage of MO decolourisation are 62.6 and 61.3, respectively. Significant decrease of decolourisation in second cycle is primarily due to significant decrease of MO intercalation in the interlayer region of ZnAl-CoW$_{12}$. As expected, this decrease is marginal from second to third or subsequent cycles. The above results indicate that the catalytic system (ZnAl-CoW$_{12}$ + H_2O_2) has potential for repetitive use without any noticeable decrease in decolourisation activity for organic dyes like MO. Analyses of reactant solution after each catalytic run by Atomic absorption spectroscopy (AAS) do not show any detectable cobalt content in the solution indicating the CoW$_{12}$ in the interlayer is quite stable and the LDH is proved to be a suitable host for heterogenisation of catalytically active species like CoW$_{12}$. The catalytic activity of ZnAl-CoW$_{12}$ can be further extended for decolourisation of other organic dyes.

Oxidation of benzaldehyde

The catalytic efficiency of ZnAl-CoW$_{12}$ was also assessed for hydrogen peroxide mediated oxidation of benzaldehyde to benzoic acid. The results obtained under varying reaction temperature, amount of catalyst, volume of H_2O_2 and reaction time is presented in Figure 7a-d. At first the reaction was carried out for 1.0 h to optimize the other parameters like reaction temperature, amount of catalyst and H_2O_2. It is evident from Figure 7a that the conversion of benzaldehyde (10.2 mL, 89.7 mM) with a fixed dose of catalyst (0.1 g) and H_2O_2 (20 mL of 30%) increases with increasing temperature, reaches to a maximum value at ~ 80-90°C and then decreases marginally on further increase of temperature. On variation of H_2O_2 (10-40 mL), keeping the other parameters constant, the activity (Figure 7b) is found increase up to 20 mL and there after practically remains constant on further increase of H_2O_2. The results of variation of amount of ZnAl-CoW$_{12}$ in the range (0.05 to 0.2 g) again shows (Figure 7c) an increasing trend up to 0.1 g catalyst dose but decreases at higher dose of catalyst presumably due to partial decomposition of H_2O_2 by catalyst causing a decrease in its concentration. Keeping the reaction temperature, catalyst dose and H_2O_2 volume fixed at 90 ºC, 0.1 g and 20 mL, respectively, the reaction time was optimized. The variation of reaction time in between 1-6 h shows that the conversion of benzaldehyde increases with increase of time, reaches to a maximum value in ~ 4 h. Further increase in time course of reaction does not lead to any increase in conversion of benzaldehyde. Under these optimize set of conditions (benzaldehyde, 10.2 mL; H_2O_2, 20 mL; ZnAl-CoW$_{12}$, 0.10 g; Reaction temperature, 90 ºC and reaction time, 4 h), the conversion of benzaldehyde is found to be ~ 86.6 %.
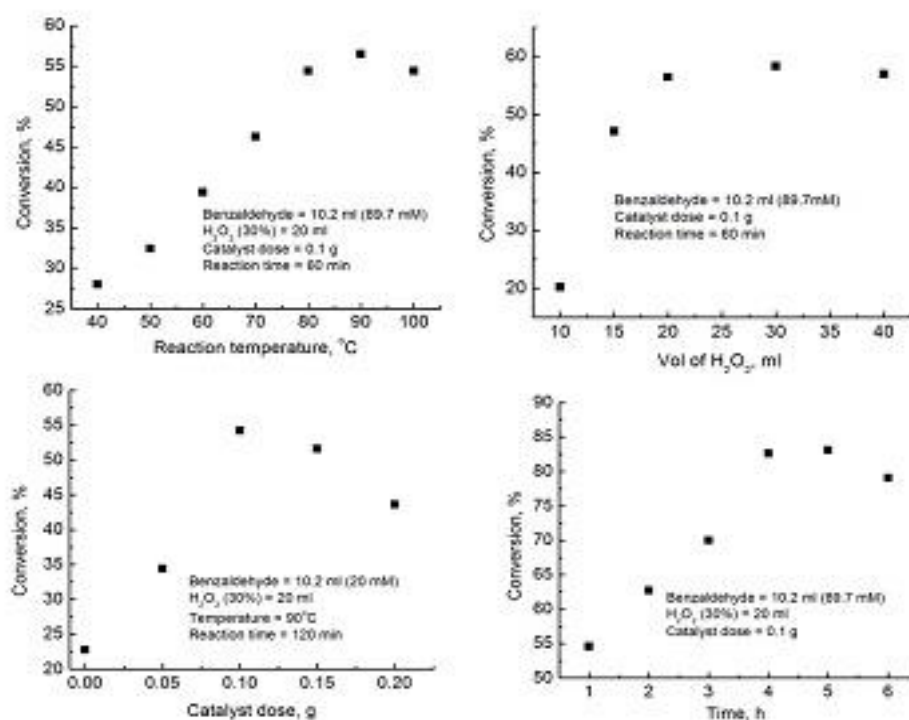
Figure 7. Effect of (a) reaction temperature (40–100 ºC) and (b) H_2O_2 amount (10–40 ml) on the oxidation of benzaldehyde. Effect of (c) catalyst amount (0.05–0.2 g) and (d) reaction time (1–6 h) on the oxidation of benzaldehyde.

This values is lower than that reported (98.8%) for the same reaction using MgAl-CoW$_{12}$ as the catalyst primarily due to intercalation of relatively higher amount of CoW$_{12}$ in the interlayer of MgAl-LDH (68.7 wt. %) as against 56.2 wt. % in the present case.[14] It is worth noting that the conversion of benzaldehyde under identical conditions with either ZnAl-CO$_3$ (0.1 g) or equivalent amount (0.58 g) of neat CoW$_{12}$ in presence of H_2O_2 (20 mL 30 %) is only 27 % and 48 %, respectively. Similarly, the conversion of benzaldehyde (10.2 mL) by H_2O_2 (20 mL) and without ZnAl-CoW$_{12}$ is only 30.5 %. While with ZnAl-CoW$_{12}$ (0.10 g) alone without H_2O_2, the conversion of benzaldehyde is less than 5 %. The above observation shows that there is a significant improvement in the catalytic activity of CoW$_{12}$ when intercalated in the interlayer of ZnAl-LDH. Moreover, the loss of CoW$_{12}$ after the reaction can be avoided.
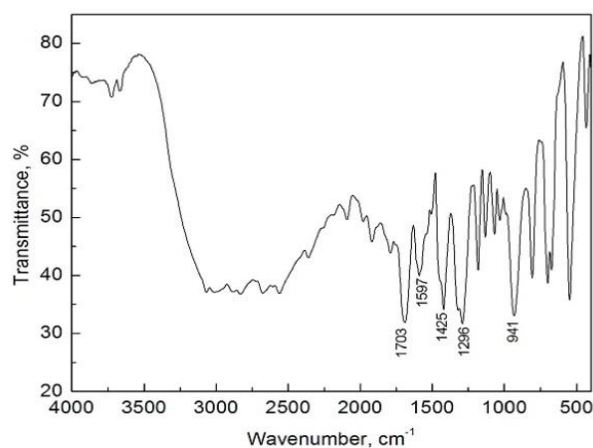

Figure 8. FT-IR spectra of oxidation product of benzaldehyde.

The formation of benzoic acid as the oxidation product of benzaldehyde is evident from melting point measurement (122–124 °C) and FT-IR spectra (Figure 8). The bands at 1703 and 1296 cm^{-1} are attributed to >C=O and − OH group, respectively. The absorption bands in between 900-1100 cm^{-1} are attributed to the benzene ring or to the carbon-oxygen bond of the acid grouping.

Conclusions

A catalytically active polyoxometallate (Co^{III}W$_{12}$O$_{40}$$^{5-}$) was successfully intercalated in the interlayer of ZnAl-LDH through rehydration of its calcined product at ambient temperature under N$_2$ atmosphere. Physicochemical characterization by various methods indicated the intercalation of Co^{III}W$_{12}$O$_{40}$$^{5-}$ in the interlayer region of LDH. The intercalated material was found active for oxidative decolourisation of methyl orange as well as conversion of benzaldehyde to benzoic acid in presence of H_2O_2.

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