



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

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Tungstocobaltate, $(\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40})^{5-}$, intercalated ZnAl-layered double hydroxide (ZnAl-CoW₁₂) 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 $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ (58 wt. %) in the interlayer of LDH. The catalytic activity of ZnAl-CoW₁₂ was evaluated for hydrogen peroxide mediated decolourisation of methyl orange and oxidation of benzaldehyde to benzoic acid under varying reaction conditions. ZnAl-CoW₁₂ was found effective for both the reactions and stable under the experimental conditions for repetitive use without any noticeable decrease in activity.

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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.

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 H₂O₂ 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, $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ (CoW₁₂),^{14,26} in the interlayer of

Experimental

Synthesis of materials

ZnAl-LDH (molar ratio of Zn/Al = 3) was prepared by coprecipitation of mixed aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 tungstocobaltate, $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}] \cdot 20\text{H}_2\text{O}$, was synthesized following the reported method^{25,27} and its purity was checked by spectral analysis.

(CoW₁₂) ion was intercalated in the interlayer LDH through rehydration of calcined LDH in presence desired amount of aqueous solution of $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}] \cdot 20\text{H}_2\text{O}$. In typical lot a weighed amount of ZnAl(O) was dispersed in 50 mL of aqueous solution of $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]$ (0.52 g) and the pH was adjusted to ca. 6.5 with dilute HNO₃ solution. The mixture was then stirred under N₂ atmosphere for ~ 4 h. By this time the initial green colour of the solution was changed to colourless indicating almost complete intercalation of tungstocobaltate 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 CoW₁₂ intercalated sample was denoted as ZnAl-CoW₁₂.

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 $2^\circ(2\theta)/\text{min}$ using Ni filtered $\text{CoK}\alpha$ (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 $10^\circ\text{C min}^{-1}$. 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 (Merck, GR) in deionized distilled water and was diluted to desired concentration as and when required. H_2O_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_2O_2 and ZnAl-CoW_{12} in a 100 mL conical flask were mechanically shaken in thermostated water bath shaker at $30\pm 0.2^\circ\text{C}$. 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 ($\epsilon = 2.68\times 10^4\text{ M}^{-1}\text{ cm}^{-1}$) to evaluate the concentration of residual MO. In aqueous solution, MO is almost completely dimerised above $2\times 10^{-4}\text{ M}$ and undergoes further aggregation at millimolar and higher concentrations²⁹. Hence, the concentration of MO was kept $< 1\times 10^{-4}\text{ M}$ 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_2O_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_2O_2 in a 100 mL flask was heated under stirring condition to initiate the reaction. The reaction time, temperature and amounts of H_2O_2 and catalyst were varied to optimize the reaction parameters. The formation of benzoic acid is evident from its isolation by similar method described earlier¹⁴ 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 $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 20\text{H}_2\text{O}$ 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 $[\text{Zn}_{0.74}\text{Al}_{0.26}(\text{OH})_2](\text{CO}_3)_{0.146}$ and $[\text{Zn}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CoW}_{12}\text{O}_{40})_{0.045}(\text{CO}_3)_{0.012}$, 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 $\text{CO}_3^{2-}/\text{OH}^-$ ions. The wt. % of CoW_{12} in ZnAl-CoW_{12} is ~ 56.2 which is $\sim 12\%$ 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 ($\text{Mg}/\text{Al} = 2$) sample, used for intercalation, than ZnAl-LDH ($\text{Zn}/\text{Al} \approx 3$).

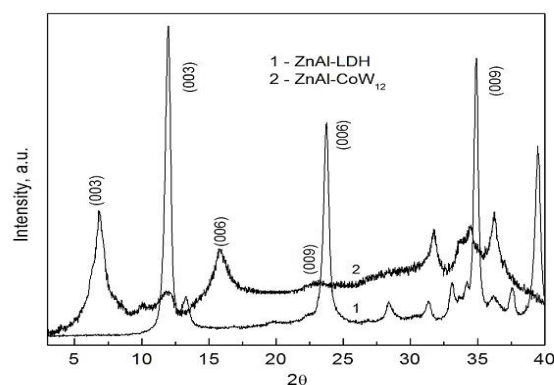


Figure 1. Powder XRD patterns of ZnAl-LDH and ZnAl-CoW_{12} .

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.

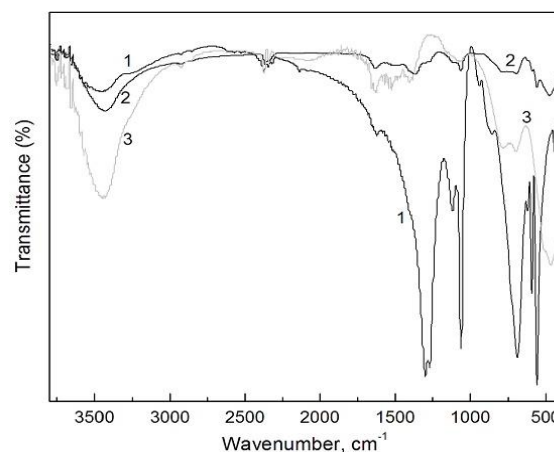


Figure 2. FT-IR spectra of calcined ZnAl-LDH (1), CoW_{12} only (2) and ZnAl-CoW_{12} (3).

The IR spectra of ZnAl-CoW₁₂ along with K₅[Co^{III}W₁₂O₄₀] and Zn(Al)O are presented in figure 2. The Keggin-type structure of [CoW₁₂O₄₀]⁵⁻ anion consists of one centrally located CoO₄ which is caged by 12 octahedral WO₆ 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 K₅[Co^{III}W₁₂O₄₀].20H₂O displayed four characteristic bands at 955, 883, 698 and 445 cm⁻¹ attributing to $\nu_{as}(W-O_d)$; $\nu_{as}(W-O_b-W)$, $\nu_{as}(W-O_c-W)$, $\nu_{as}(Co-O_a)$ or $\delta(O-Co-O)$ ^{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-CoW₁₂ are similar to that of K₅[Co^{III}W₁₂O₄₀] providing further evidence of intercalation of [CoW₁₂O₄₀]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.

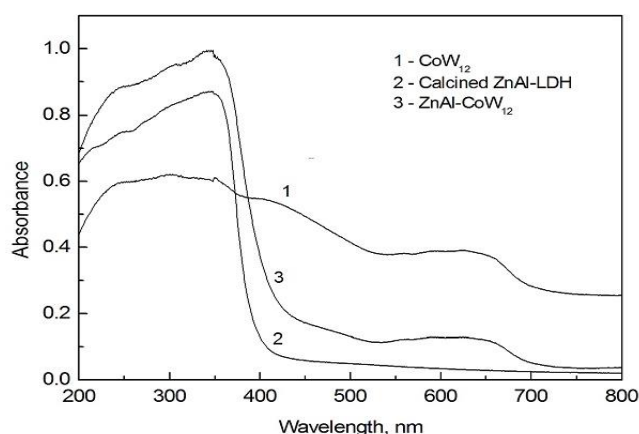


Figure 3. UV-Vis DRS ZnAl-LDH (calcined), ZnAl-CoW₁₂ and CoW₁₂.

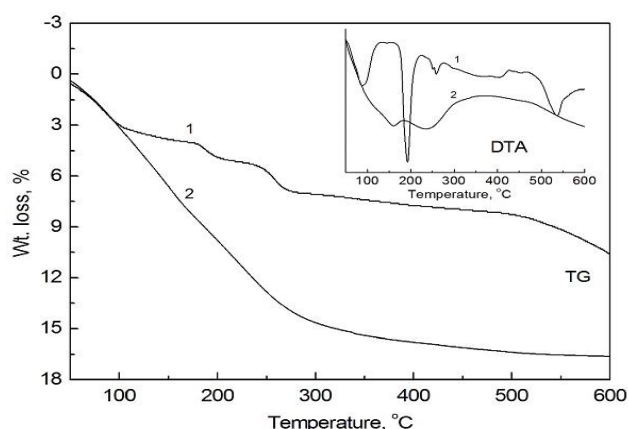


Figure 4. TG and DTA curves of CoW₁₂ (1) and ZnAl-CoW₁₂ (2) at heating rate 10°C under N₂ atmosphere.

More evidence in favour of intercalation of CoW₁₂ in the interlayer of LDH is obtained from UV-Vis DRS (Figure 3). The characteristics peaks of CoW₁₂ and ZnAl-LDH are also appeared in the case of ZnAl-CoW₁₂ indicating the intercalation of CoW₁₂ in the interlayer of ZnAl-LDH. The

TG-DTA curves of CoW₁₂ and uncalcined ZnAl-CoW₁₂ are presented in figure 4. It is seen that ZnAl-CoW₁₂ 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 CoW₁₂ to expel the produced water molecules. The neat complex also exhibits multi stage weight losses with two major endothermic peaks at 90 and 190 °C.

Catalytic activity of ZnAl-CoW₁₂

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 H₂O₂ (0.05 M) indicating there is no decolourisation of MO by H₂O₂ 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-CoW₁₂, respectively, cannot be ruled out. A typical experiment, with ZnAl-CoW₁₂ (0.5 g l⁻¹) and MO (35 μM) and without addition of H₂O₂, 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-CoW₁₂, estimated using the absorbance values of MO at 275 and 464 nm, is found to be ~ 14 %. In presence of both H₂O₂ and ZnAl-CoW₁₂, the MO peak at 275 nm is not observed (Figure 5) due to high absorbance of H₂O₂ 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 H₂O₂ is decreased with the progress of reaction.

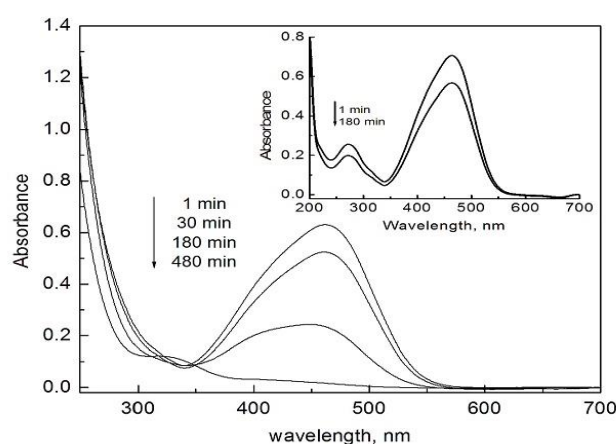


Figure 5. Successive spectral scan of MO (35 μM) with time in presence of ZnAl-CoW₁₂ (0.5 g/l) and H₂O₂ (0.05 M). (Inset) in presence of ZnAl-CoW₁₂ (0.5 g/l) only.

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 H₂O₂ is presented in figure 6. It is seen that the decolourisation of MO is strongly catalysed in presence of both H₂O₂ and catalytic amount of ZnAl-CoW₁₂ and more than 80 % MO (35 μM) is decolourised against 14 % decolourisation in the absence of H₂O₂. The decolourisation data up to 300 min are subjected to non-linear least square fitting (eqn. 1).

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

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.

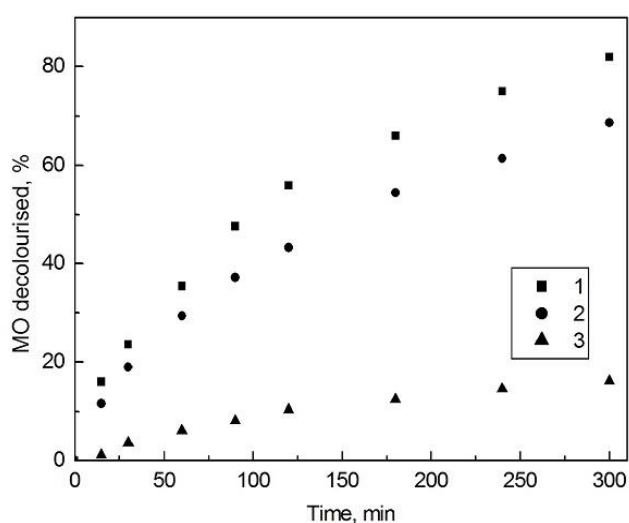


Figure 6. Time course of MO decolourisation in presence of ZnAl-CoW₁₂ (0.5 g/l) and [H₂O₂] = 0.02 M at varying MO concentrations: (1) 35 μM, (2) 60 μM and MO decolourisation (35 μM) by ZnAl-CoW₁₂ (0.5 g/l) without H₂O₂.

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

[H ₂ O 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 °C.

The effect of initial H₂O₂ 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 H₂O₂. The decrease of oxidation activity of H₂O₂ at higher concentration is most likely due to increase of catalysed H₂O₂ 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-CoW₁₂ for repetitive use, the reactant solution was charged with desired amount of MO and H₂O₂ after every 5 h to maintain the same initial MO (35 μM) and H₂O₂ (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-CoW₁₂ dose of 0.50 g L⁻¹. In the second round with a fresh load of MO and H₂O₂, 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-CoW₁₂. As expected, this decrease is marginal from second to third or subsequent cycles. The above results indicate that the catalytic system (ZnAl-CoW₁₂ + H₂O₂) 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 CoW₁₂ in the interlayer is quite stable and the LDH is proved to be a suitable host for heterogenisation of catalytically active species like CoW₁₂. The catalytic activity of ZnAl-CoW₁₂ can be further extended for decolourisation of other organic dyes.

Oxidation of benzaldehyde

The catalytic efficiency of ZnAl-CoW₁₂ 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 H₂O₂ 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 H₂O₂. 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 H₂O₂ (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 H₂O₂ (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 H₂O₂. The results of variation of amount of ZnAl-CoW₁₂ 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 H₂O₂ by catalyst causing a decrease in its concentration. Keeping the reaction temperature, catalyst dose and H₂O₂ volume fixed at 90 °C, 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; H₂O₂, 20 mL; ZnAl-CoW₁₂, 0.10 g; Reaction temperature, 90 °C and reaction time, 4 h), the conversion of benzaldehyde is found to be ~ 86.6 %.

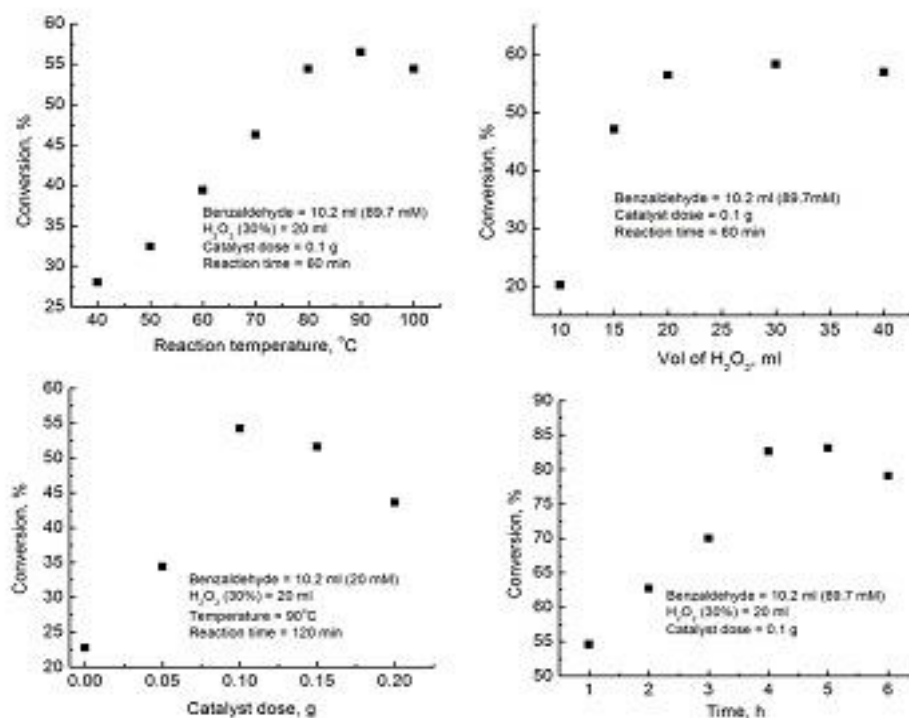


Figure 7. Effect of (a) reaction temperature (40–100 °C) and (b) H₂O₂ amount (10–40 ml) on the oxidation of benzaldehyde. Effect of (c) catalyst amount (0.05–0.2 g) and (d) reaction time (1–6 h) on the oxidation of benzaldehyde.

This value is lower than that reported (98.8%) for the same reaction using MgAl-CoW₁₂ as the catalyst primarily due to intercalation of relatively higher amount of CoW₁₂ 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-CO₃ (0.1 g) or equivalent amount (0.58 g) of neat CoW₁₂ in presence of H₂O₂ (20 mL 30 %) is only 27 % and 48 %, respectively. Similarly, the conversion of benzaldehyde (10.2 mL) by H₂O₂ (20 mL) and without ZnAl-CoW₁₂ is only 30.5 %. While with ZnAl-CoW₁₂ (0.10 g) alone without H₂O₂, the conversion of benzaldehyde is less than 5 %. The above observation shows that there is a significant improvement in the catalytic activity of CoW₁₂ when intercalated in the interlayer of ZnAl-LDH. Moreover, the loss of CoW₁₂ after the reaction can be avoided.

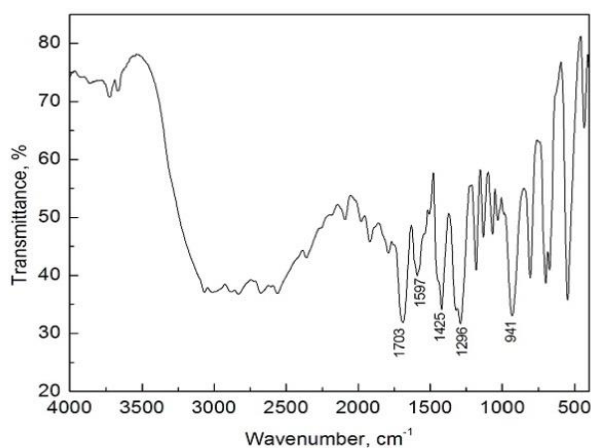


Figure 8. FT-IR spectra of oxidation product of benzaldehyde.

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}W₁₂O₄₀⁵⁻) was successfully intercalated in the interlayer of ZnAl-LDH through rehydration of its calcined product at ambient temperature under N₂ atmosphere. Physicochemical characterization by various methods indicated the intercalation of Co^{III}W₁₂O₄₀⁵⁻ 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 H₂O₂.

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