# Tungstocobaltate-pillared layered double hydroxides: Preparation, characterization, magnetic and catalytic properties

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## ABSTRACT

A new polyoxometalate anion-pillared layered double hydroxide (LDH) was prepared by aqueous ion exchange of a Mg-Al LDH precursor in nitrate form with the tungstocobaltate anions $[CoW_{12}O_{40}]^{5-}$. The physicochemical properties of the product were characterized by the methods of powder X-ray diffraction, elemental analysis, infrared spectroscopy, thermogravimetric analysis and cyclic voltammetry. It was confirmed that $[CoW_{12}O_{40}]^{5-}$ was intercalated between the brucite-type layers of the LDHs without a change in the structure. Magnetic measurement shows the occurrence of antiferromagnetic interactions between the magnetic centers. The investigation of catalytic performance for this sample exhibits high activity for the oxidation of benzaldehyde by hydrogen peroxide.

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## 1. Introduction

Layer double hydroxides (LDHs), known as ionic lamellar solids with positively charged layers and exchangeable hydrated gallery anions [1], have received considerable attention due to their applications in various fields, such as anion scavengers in wastewater, biomolecule reservoirs or as polymer additives to improve its properties [2–4]. The general formula for LDH is $[M_{(1-x)}^{2+}M_x^{3+} (OH)_2][A_{(x/m)}^{m-}] \cdot nH_2O$, where $M^{2+}$ and $M^{3+}$ are divalent and trivalent metal cations such as $Mg^{2+}$, $Cu^{2+}$, $Zn^{2+}$ and $Al^{3+}$, $Ga^{3+}$, $Cr^{3+}$, respectively, and $A^{m-}$ is a simple or complex organic or inorganic anion such as $Cl^-$, $NO_3^-$, $CO_3^{2-}$ or $C_8H_4O_4^{2-}$ [5]. The most attractive characteristic of LDHs is the anionic exchange property such that a wide range of organic or inorganic guests have been incorporated into LDHs [6].

Polyoxometalates (POMs) [7,8], as anionic early-transition-metal oxide clusters formed by linked oxygen octahedra coordinating transition metals (V, Mo W, etc.), are a fascinating class of compounds which have a definite size and shape and resemble a metal–oxygen cluster structure, possessing many properties that make them attractive for applications in catalysis, biology, magnetism, optics and medicine [9]. Since the first example of POM-pillared LDHs was used as exhaust gas and hydrocarbon conversion catalysts [10], POMs have been proved to be the most attractive

interlayer pillaring species suitable for material applications such as shape-selective adsorption and catalysis [11–13], such as photooxidation of isopropyl alcohol to acetone, shape-selective epoxidation of alkenes and selective oxidation of o-xylene to o-tolualdehyde. As a result, a huge number of iso- and heteropolyanions with different nuclearities and structures have been incorporated into the interlayer of these materials later [14–25]. To develop new POM-pillared LDHs with multifunctional properties, we attempt to use polyanion $[CoW_{12}O_{40}]^{5-}$ as the exchange agent considering the strong oxidizing ability of Co (III) cation [26]. The Keggin-type structure of $[CoW_{12}O_{40}]^{5-}$ anion is composed of one Co (III) ion surrounded by four oxygen ions to form a tetrahedron. The Co (III) ion is located centrally and caged by 12 octahedral $WO_6$ units linked to one another by the neighboring oxygen atoms. There are a total of 24 bridging oxygen atoms that link the 12 W atoms. The W centers in the 12 octahedra are arranged on a sphere almost equidistant from each other, in four $W_3O_{13}$ units, giving the complete structure an overall tetrahedral symmetry. Here, we report the preparation and characterization of a new tungstocobaltate anion-pillared layered double hydroxide $[Mg_2Al(OH)_6]_5[CoW_{12}O_{40}] \cdot 26H_2O$ (MgAl-CoW$_{12}$). The materials thus prepared were well characterized by elemental analyses, powder X-ray diffraction (PXRD), IR spectroscopy, thermogravimetric (TG) and differential thermal analyses (DTA), and their electrochemical behavior and magnetic properties were investigated and compared with those of the precursor anion. Also, a primary investigation of the catalytic activity of MgAl-CoW$_{12}$ shows an excellent catalysis for oxidation of benzaldehyde to benzonic acid.

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## 2. Experimental

### 2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Co, W, Mg and Al were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained in the range 400–4000 $cm^{-1}$ on the Alpha centaure FT/IR spectrophotometer using KBr pellets. The PXRD analyses were performed with a Rigaku D/max-3c X-ray diffract-ometer, using Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing $N_2$ at a heating rate of 10 °C min$^{-1}$. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at room temperature. A conventional three-electrode cell, consisting of a modified carbon paste electrode (CPE) as the working electrode, a Ag/AgCl reference electrode and a Pt gauze counter electrode, was used. The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-5 SQUID magnetometer in the temperature range 2–300 K and magnetic field up to 5 T. Diamagnetic corrections were estimated from Pascal's constants.

### 2.2. Synthesis of $[CoW_{12}O_{40}]^{5-}$ anion-pillared layered double hydroxides

The Mg-Al LDH starting material, MgAl[NO₃] (observed formula: $Mg_{0.98}Al_{0.51}(OH)_{3.1}(NO_3)_{0.48} \cdot 1.54H_2O$), was prepared as described previously [25] and characterized by PXRD analysis. $K_5[Co^{III}W_{12}O_{40}] \cdot 20H_2O$ was prepared according to the literature method [27] and characterized by IR spectra analysis. Anion-exchange reactions with $[CoW_{12}O_{40}]^{5-}$ anions were carried out with an aqueous slurry of MgAl[NO₃]. Under an $N_2$ atmosphere, 50 ml of $K_5[CoW_{12}O_{40}]$ (0.52 g) was acidified to a pH value of 6.5 with 0.20 M HNO₃ solution. The mixture was kept under nitrogen and refluxed in the temperature range of 90–95 °C for 10 h. The resulting solid was filtered and washed with boiling water and hot ethanol three times, and then dried in vacuum at 70 °C overnight (see Scheme 1).

### 2.3. Preparation of a MgAl-CoW₁₂ LDH-modified carbon paste electrode (CPE)

MgAl-CoW₁₂-modified CPE was fabricated as follows: 0.5 g graphite powder and 0.05 g MgAl-CoW₁₂ were mixed, and ground together by an agate mortar and pestle to obtain an even, dry mixture; 0.50 ml paraffin oil was added to the mixture and stirred
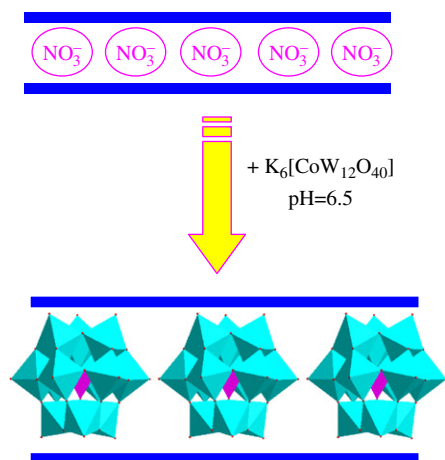
with a glass rod. Then the mixture was packed into a glass tube with a diameter of 3 mm, and the surface was pressed tightly onto weighing paper with a copper rod through the back. Electrical contact was established with a copper rod through the back of the electrode.

### 2.4. Catalytic reactions

Oxidation reactions of benzaldehyde were carried out in a 100 ml flask containing a catalyst (0.1 g MgAl-CoW₁₂), benzalde-hyde (10.2 ml) and 30 wt% $H_2O_2$ (30 ml). The reaction mixture was heated to the target temperature and stirred for hours. Then it was cooled to room temperature, adjusted to a pH value of 10 with 15% NaHCO₃ solution and the oil layer was removed. The water layer was adjusted to pH = 2 with 1:1 $H_2SO_4$, and then stored in the refrigerator at 5 °C for 24 h. The obtained crystals were washed with washed with a saturated solution of benzoic acid three times, and then dried at a saturated solution of benzoic acid three times, and then dried at 80 °C for 4 h. The obtained benzoic acid was characterized by IR spectra analysis and melt-point measure-ments (122–124 °C) and the yield of benzoic acid was calculated by the weight of the final white crystals.

## 3. Results and discussion

### 3.1. X-ray diffraction patterns

The powder XRD patterns obtained for the starting material MgAl-NO₃ and the pillared derivative MgAl-CoW₁₂ are shown in Fig. 1. It shows that the absence of the diffraction peaks attributed to the LDH containing $NO_3^-$ anion and the appearance of several new ones with the reflections shifted to lower $2\theta$ values due to the LDH with CoW₁₂ as intercalate anions, which indicates successful ion exchange of nitrate ions for CoW₁₂. It is well known that the first basic reflection corresponding to the highest $d$-value gives information about the interlayer distance. Considering the layer thickness of the MgAl-LDH to be 0.48 nm, the gallery height of MgAl-CoW₁₂ is obtained as 1.01 nm, calculated by subtracting the layer thickness from the (001) reflection (1.49 nm), which is in accordance with the van der Waals diameter (1.02) estimated from crystallographic data for a Keggin ion salt [28]. To optimize
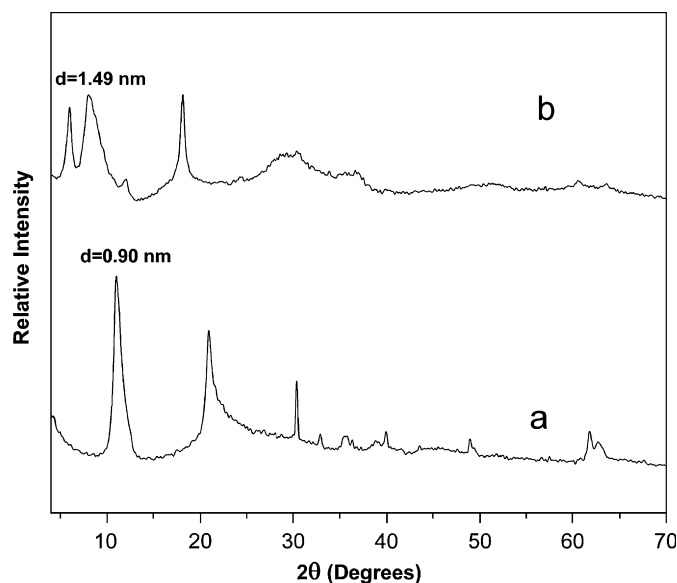


Scheme 1. Synthesis route of POMs-pillared layered double hydroxides.



Fig. 1. X-ray diffraction pattern of (a) MgAl-NO₃, (b) MgAl-CoW₁₂.

the H bonding among the POM oxygen atoms and the gallery hydroxyl groups, the interlayer $\alpha$-CoW$_{12}$O$_{40}^{5-}$ ions most likely adopt the C$_2$ ($\perp$) orientation [11]. Compared with the XRD data of MgAl-LDH, the appearance of diffraction peaks with lower 2$\theta$ values in the XRD data of MgAl-CoW$_{12}$ implies that the interlayer distances increased obviously after the intercalation of CoW$_{12}$ anions. However, the several broadened diffraction peaks in the XRD data of MgAl-CoW$_{12}$ indicate the decreasing crystallinity due to the formation of MgAl-CoW$_{12}$. While the MgAl-LDH precursor emerged as a well-crystallized material, the exchanged MgAl-CoW$_{12}$ yielded relatively broader peaks.

## 3.2. IR spectroscopy

The IR spectra of K$_5$[CoW$_{12}$O$_{40}$] and of the layered compounds MgAl-NO$_3$ and MgAl-CoW$_{12}$ are shown in Fig. 2. The bands at 3598 and 1617 cm$^{-1}$ for K$_5$[CoW$_{12}$O$_{40}$] are attributed to the hydroxyl groups' stretching vibration and the bending mode of water molecules, and it displays the characteristic features of a Keggin-type structure at 959, 885, 759, 670 and 441 cm$^{-1}$ for $\nu$ (W$=$O), $\nu$ (W–O–W) and $\nu$ (Co–O), respectively, which is in agreement with the results reported previously [29]. The spectra of MgAl-CoW$_{12}$-LDH are similar to that of K$_5$[CoW$_{12}$O$_{40}$], which suggests that the structure of the [CoW$_{12}$O$_{40}$]$^{5-}$ ions is retained in the pillared derivative MgAl-CoW$_{12}$. 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, and the peak at 1380 cm$^{-1}$ due to the nitrate band disappeared in the MgAl-CoW$_{12}$ sample, suggesting that the anion exchange was complete.

## 3.3. Elemental analysis and thermogravimetry

In agreement with the XRD and IR results, elemental analysis of the MgAl-CoW$_{12}$-LDH composites confirms the intercalation of the polyoxoanions into the layered double hydroxides. The interlayer water molecules were determined by TGA after the sample was dried at 100 °C for 2 h. Based on the analytical data, approximate compositions for MgAl-CoW$_{12}$-LDH were determined and are shown in Table 1.
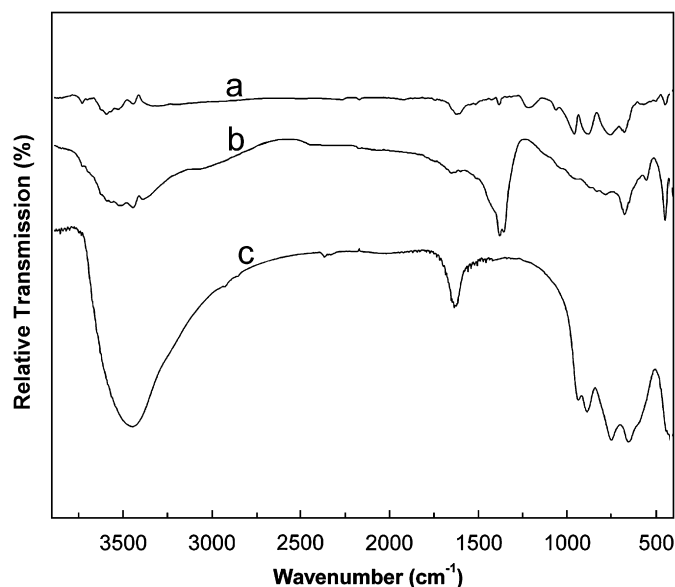
**Fig. 2.** Infrared spectra of (a) K$_5$[CoW$_{12}$O$_{40}$], (b) MgAl-NO$_3$, (c) MgAl-CoW$_{12}$.

**Table 1**
Chemical compositions for the LDH samples

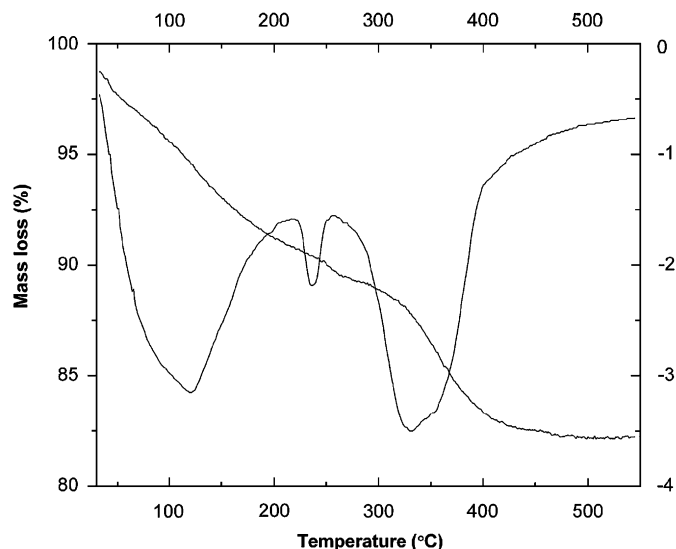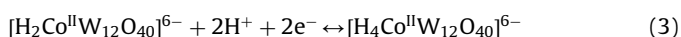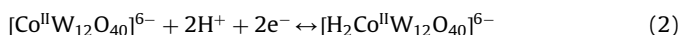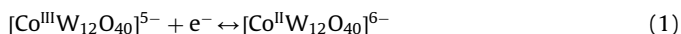| Chemical formula (cacl.) | Formula (obse.) |
| --- | --- |
| Mg$_2$Al-NO$_3$ | Mg$_{0.98}$Al$_{0.51}$(OH)$_{3.1}$(NO$_3$)$_{0.48}$ · 1.54H$_2$O |
| Mg$_2$Al-(CoW$_{12}$)$_{0.2}$ | Mg$_{1.03}$Al$_{0.49}$ (OH)$_{3.0}$[CoW$_{12}$O$_{40}$]$_{0.11}$ · 2.60H$_2$O |

[a] Atomic ratios with respect to Al.

**Fig. 3.** TG and DTA curve of MgAl-CoW$_{12}$.

The TG and DTA curves recorded for the MgAl-CoW$_{12}$ LDH sample are shown in Fig. 3. Three endothermic effects can be distinguished in the DTA curve. The first endothermic peak at 120 °C is due to the loss of surface-adsorbed water and the second effect at 236 °C is ascribed to the removal of interlayer water. The last peak recorded at 330 °C corresponds to a collapse of the layered structure. The weight loss at 330–440 °C resulted from both the dehydroxylation of MgAl–LDH layers and the decomposition of CoW$_{12}$ to expel the produced water molecules. The TG curve shows that the structural water loss occurred in different steps with ca. 11% of the total weight, which corresponded to 2.6 water molecules as per the observed formula.

## 3.4. Cyclic voltammetry

The electrochemical behavior of MgAl-CoW$_{12}$ was investigated by using a CPE as the working electrode in 2 M H$_2$SO$_4$ solution. As shown in Fig. 4, it exhibits one reversible one-electron (A1′/C1′, 924/847 mV) and two two-electron redox processes (A2′/C2′, −183/−295 mV; A3′/C3′ −287/−405 mV) corresponding to Co$^{3+}$/Co$^{2+}$ couple and W waves, respectively [13]. These processes can be expressed as follows:

$$[Co^{III}W_{12}O_{40}]^{5-} + e^- \leftrightarrow [Co^{II}W_{12}O_{40}]^{6-} \tag{1}$$

$$[Co^{II}W_{12}O_{40}]^{6-} + 2H^+ + 2e^- \leftrightarrow [H_2Co^{II}W_{12}O_{40}]^{6-} \tag{2}$$

$$[H_2Co^{II}W_{12}O_{40}]^{6-} + 2H^+ + 2e^- \leftrightarrow [H_4Co^{II}W_{12}O_{40}]^{6-} \tag{3}$$

It is similar to the electrochemical behavior of pure K$_5$[Co$^{III}$W$_{12}$O$_{40}$] observed in 2 M H$_2$SO$_4$ solution (A1/C1, 1015/916 mV; A2/C2, −174/−228 mV; A3/C3 −280/−345 mV), which also indicates that the [CoW$_{12}$O$_{40}$]$^{5-}$ ions were successfully incorporated into the space of Mg-Al LDH.
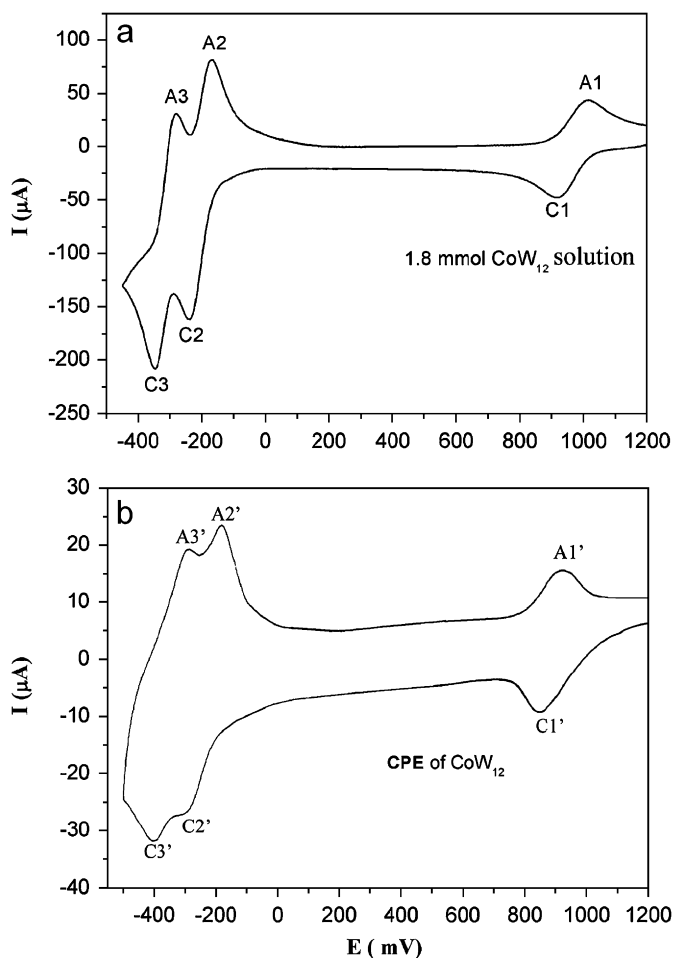
**Fig. 4.** (a) Cyclic voltammogram of $K_5[CoW_{12}O_{40}]$ in 2 M $H_2SO_4$ solution. (b) Cyclic voltammogram of the carbon paste electrode (CPE) in 2 M $H_2SO_4$ aqueous solution for MgAl-$CoW_{12}$.



**Fig. 5.** Plots of $\chi_m$ (circle dot) and $\chi_m T$ (triangle dot) vs. $T$ for a powder sample of MgAl-$CoW_{12}$.
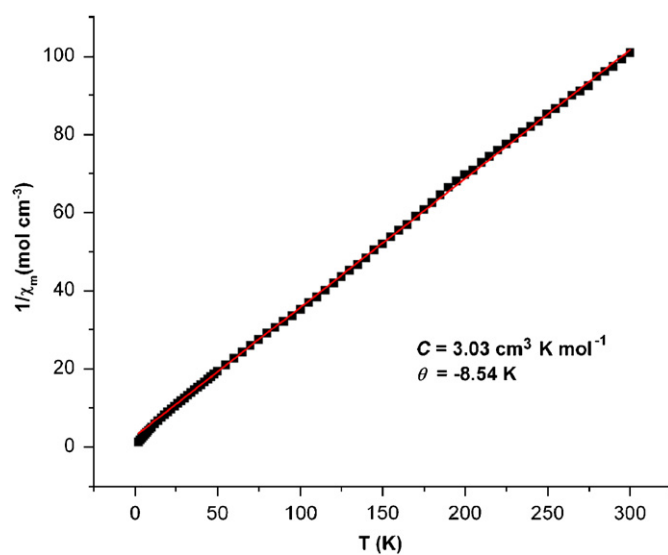


**Fig. 6.** Inverse of the molar magnetic susceptibility of MgAl-$CoW_{12}$ vs. temperature.

## 3.5. Magnetic properties

The temperature dependence of magnetic susceptibility $\chi_m$ for MgAl-$CoW_{12}$ compound **1** is investigated in the range 2–300 K with an applied field of 1000 Oe (Fig. 5). Upon cooling of the sample, the $\chi_m$ value increases, reaching a maximum of 0.73 cm$^3$ K mol$^{-1}$ at 2.0 K. The $\chi_m T$ value remain basically at 2.97 cm$^3$ K mol$^{-1}$(per mol Co$^{3+}$) from room temperature down to about 100 K, slightly less than the expected value (3.00 cm$^3$ K mol$^{-1}$) for one non-interacting Co(III) center with $S = 2$, and then slowly declines to 1.12 cm$^3$ K mol$^{-1}$ at 2 K indicating a typical curve shape of the occurrence of an antiferromagnetic interaction between the magnetic transition metal ions. The $1/\chi_m$ versus $T$ plot (see in Fig. 6) could be fit with the Curie–Weiss equation from 100 to 300 K, yielding $C = 3.03$ cm$^3$ K mol$^{-1}$ and $\theta = -8.54$ K; the negative Weiss constant indicates a weak antiferromagnetic coupling between Co$^{3+}$ centers. The interactions between the magnetic centers could be affected by the ordered arrangement of the anions in the layer space of LDHs.

## 3.6. Primary investigation on catalytic activity

The catalytic activity of MgAl-$CoW_{12}$ was tested by the reaction of oxidation of benzaldehyde with hydrogen peroxide. The effects of reaction temperature, amount of catalyst, volume of
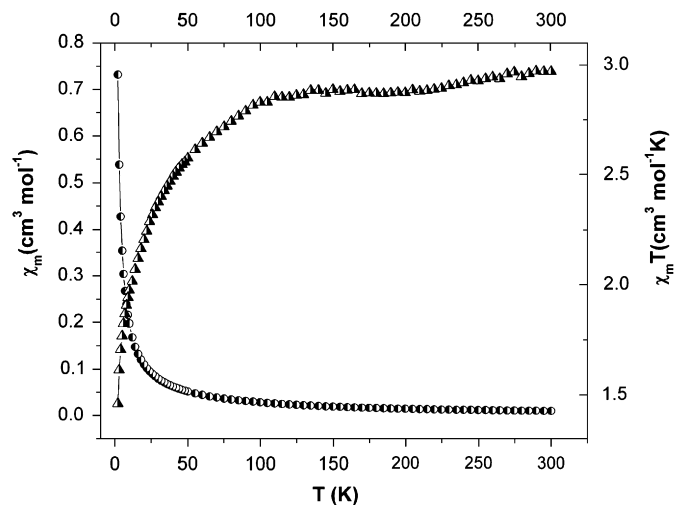
hydrogen peroxide and reaction time on the yield of benzoic acid have been investigated. The effect of reaction temperature on the oxidation of benzaldehyde (10.2 ml) by hydrogen peroxide (30 ml) in water over MgAl-[$CoW_{12}$](0.10 g) for 1 h is shown in Fig. 7a. As the reaction temperature increased, the conversion increased. But when the temperature was higher than 90 °C, the selectivity for benzaldehyde decreased leading to the reduced conversion.

The influence of the amount of catalyst on the oxidation of benzaldehyde by hydrogen peroxide over MgAl-[$CoW_{12}$] at 90 °C for 1 h is shown in Fig. 7b. As the amount of MgAl-[$CoW_{12}$] increased, the conversion of benzaldehyde increased during the reaction. However, when the amount of MgAl-[$CoW_{12}$] exceeded 0.10 g, the conversion began to decrease, which indicates that the excess catalyst may result in the decomposition of $H_2O_2$. As can be seen in Fig. 7c, as the hydrogen peroxide increased, the conversion of benzaldehyde increased and reached the maximum value on adding 30 ml $H_2O_2$.

The effect of reaction time on the oxidation of benzaldehyde (10.2 ml) over the MgAl-[$CoW_{12}$] (0.10 g) catalyst by hydrogen peroxide (30 ml) at 90 °C is shown in Fig. 7d. With increasing
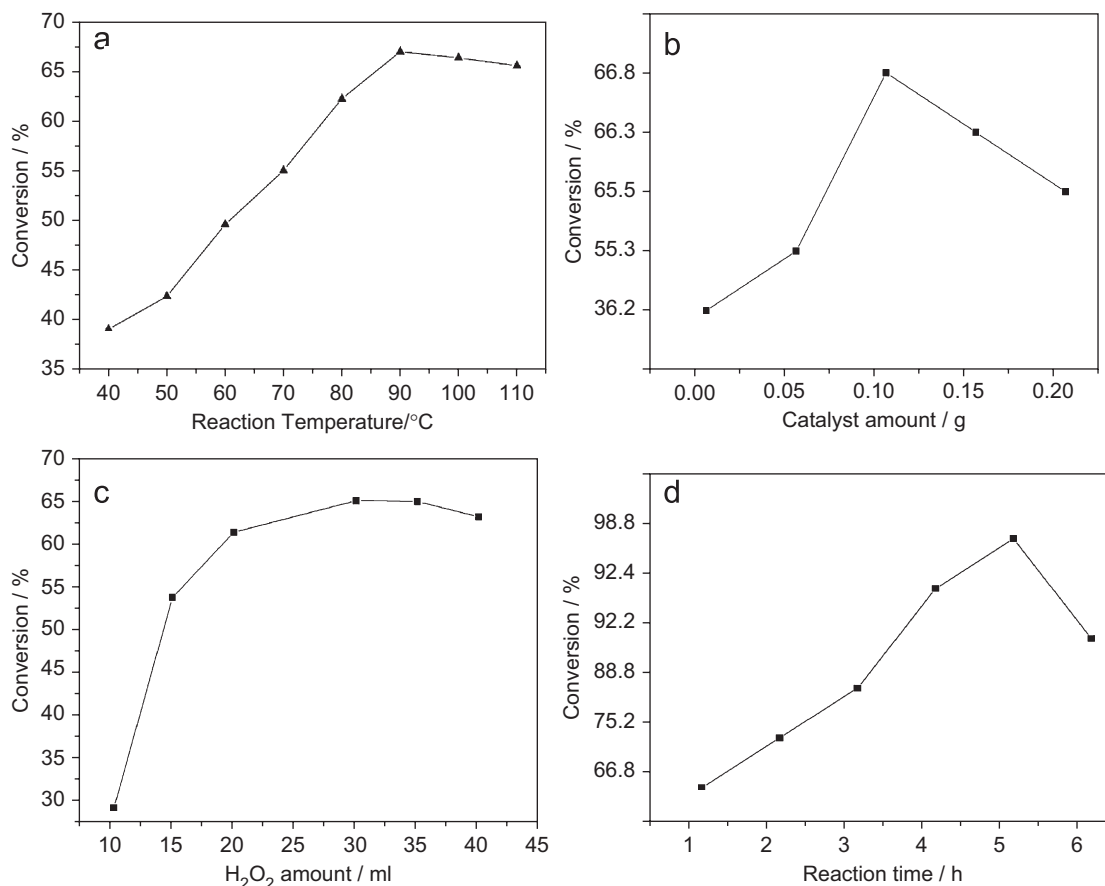
**Fig. 7.** Effect of (a) reaction temperature (40–110 °C); (b) catalyst amount (0.05–0.2 g); (c) $H_2O_2$ amount (10–40 ml); and (d) reaction time (1–6 h) on the oxidation of benzaldehyde by hydrogen peroxide.

**Table 2**
The influence on the oxidation of benzaldehyde over different catalysts by hydrogen peroxide at 90 °C for 5 h

| Catalyst | MgAl-NO$_3$ | K$_5$[CoW$_{12}$O$_{40}$] | MgAl-CoW$_{12}$ |
|---|---|---|---|
| Yield % | 75 | 77 | 98.8 |

reaction time, the yield of benzoic acid increased obviously and reached a high conversion of 98.8% at 5 h. When the reaction time is longer than 5 h, the conversion begins to drop, which might result from an unknown by-reaction.

In general, the above results indicated that MgAl-[CoW$_{12}$] is an excellent catalyst for oxidation of benzaldehyde to benzonic acid. The most optimal reaction conditions are: benzaldehyde, 10.2 ml; hydrogen peroxide, 30 ml; MgAl-[CoW$_{12}$], 0.10 g; reaction temperature, 90 °C; and reaction time, 5 h; and the maximum conversion of benzaldehyde is 98.8%. Compared with the pure K$_5$[CoW$_{12}$O$_{40}$] and MgAl-NO$_3$, the catalytic activity is considerably improved when the [CoW$_{12}$O$_{40}$]$^{5-}$ ions are intercalated into the interlayer of LDHs (see Table 2).

## 4. Conclusions

A new type of Co$^{3+}$-containing layered double hydroxide intercalated by tungstocobaltates was synthesized by treating the layered double hydroxide intercalated by the Keggin-type POM anion [CoW$_{12}$O$_{40}$]$^{5-}$. Powder XRD, together with IR, TG and cyclic voltammetry, strongly indicates that the guest anions were intercalated in the resultant material. Magnetic measurements exhibit weak antiferromagnetic interactions between the magnetic centers, which suggested that optimization of this strategy could lead, in the near future, to the preparation of molecule-based magnets inserted into solid-state materials. Also, the study of catalytic properties of the sample exhibits high activity for the oxidation of benzaldehyde with the hydrogen peroxide.

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