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# Liquid phase selective oxidation of veratryl alcohol to veratraldehyde using pure and Mg-doped copper chromite catalysts

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Mg-doped copper chromite ( $\text{CuCr}_{2-x}\text{Mg}_x\text{O}_4$ ) nanocomposites were synthesised through conventional technique. The pure and doped  $\text{CuCr}_{2-x}\text{Mg}_x\text{O}_4$  ( $x = 0.00-0.1, 0.2$  and  $0.3\%$ ) nanocomposites were characterized in terms of their morphology, crystal structure, surface area and catalytic performance. The chemical composition of  $\text{CuCr}_{2-x}\text{Mg}_x\text{O}_4$  was confirmed via FT-IR. The formation of pure and doped catalysts was validated by XRD results. TEM/SEM confirmed the formation of  $\text{CuCr}_{2-x}\text{Mg}_x\text{O}_4$  nanoparticles. Mg-doped samples possess a high specific surface area compared to pure  $\text{CuCr}_2\text{O}_4$ . Thus, the effects of temperature, solvent, time, oxidant and the amount of catalyst on the oxidation of veratryl alcohol were reported. Furthermore, detailed mechanisms of the catalytic oxidation of veratryl alcohol as well as the reusability and stability of the nanomaterial were investigated. The resulting composites were shown to be effective heterogeneous catalysts for the oxidation of veratryl alcohol.

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## 1. Introduction

In the field of heterogeneous catalysis, sunlight-activated materials are necessary. Because nanotechnology enables control over their size and morphology, there is a correlation

between their increased efficiency and these developments. In the field of catalysis, ternary metal oxides with a spinel structure ( $\text{AB}_2\text{O}_4$ ) have demonstrated exceptional properties. Thus, metal oxides were located around the octahedral (B site) and tetrahedral (A site) positions, and the quantities, type of oxides and the location of metal cations in the crystalline structure significantly affect the chemical-physical properties of chromite materials.<sup>1,2</sup> At present, chromite materials with spinel structures are present with a face-centered lattice with the space group  $Fd3m$ , whereas  $\text{Cr}^{3+}$  cations are in octahedral positions and  $\text{Cu}^{2+}$  cations occupy tetrahedral positions.<sup>3</sup> Chromium-based catalysts exhibit good resistance to atmospheric effects, high thermal stability, optical properties, resistance to chemical corrosion, photocatalysis, catalysis *etc.* Beyond that, it is interesting to see numerous applications for ceramic materials.<sup>4</sup> The doping of divalent  $\text{Mg}^{2+}$  metal ions is primarily incorporated into A-site cations in the synthesized copper chromite materials. The stoichiometry of chemical compositions and the controlled crystallite size of chromite materials prepared via the chemical method were found to be extremely favorable for achieving good-quality products.<sup>5</sup> Copper chromates were synthesized using various methods, such as sol-gel, ceramic,<sup>6</sup> microwave and co-precipitation techniques.<sup>7</sup> New chemical methods, such as hydrothermal, sol-gel/citrate,<sup>8</sup> conventional (low-temperature method), and low-temperature solution synthesis methods, were also developed.<sup>9</sup>

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**Table 1** Sample code and sample composition with their abbreviations

Sample code	Sample composition
a	CuCr <sub>2</sub> O <sub>4</sub>
b	Mg (0.1%) CuCr <sub>2</sub> O <sub>4</sub>
c	Mg (0.2%) CuCr <sub>2</sub> O <sub>4</sub>
d	Mg (0.3%) CuCr <sub>2</sub> O <sub>4</sub>

Mg<sup>2+</sup> doped chromite based catalysts were used in the selective oxidation reaction. Also, chromite based materials were more useful in industrial and technological applications.<sup>10</sup> Selective oxidation of veratryl alcohol to carbonyl compounds (aldehyde to acid) is highly challenging.<sup>11</sup> Selective oxidation of veratryl alcohol is employed to produce several industrially valuable chemicals, such as those associated with the food and fragrance industries; veratraldehyde is a highly valued chemical that is derived from crude oil and *via* the methylation of vanillin. It is interesting to note that the industry that utilizes veratraldehyde spends as much as 100 times more on bio-based veratraldehyde than on crude oil-based veratraldehyde.<sup>12–14</sup> Herein, we synthesized citrate CuCr<sub>2</sub>O<sub>4</sub> and Mg-doped CuCr<sub>2</sub>O<sub>4</sub> *via* a conventional combustion route, followed by their morphological and structural characterisation. The chemical–physical properties of the catalysts are characterised using multiple techniques. The resulting composites were shown to be effective heterogeneous catalysts for the oxidation of veratryl alcohol.

## 2. Experimental

At present, (CuCr<sub>2</sub>O<sub>4</sub>) copper chromite spinel oxides were (flow chart 1) prepared *via* the conventional combustion route. The following chemicals, such as citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (used as fuel), chromium nitrate Cr (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, copper nitrate Cu (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and magnesium nitrate Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were used without purification. First stage (I): chromium nitrate 1 M solution and copper nitrate 0.5 M solution were prepared separately in 25 mL (DI) deionized water. Second stage (II): Cr and Cu solutions were mixed and stirred continuously for 1 h to obtain a homogenous solution. Third stage (III): An aqueous solution of 5 M citric acid was prepared in DI water, and the citrate to nitrate ratio was fixed at one. Then, the obtained solution (citrate) is dropped into the nitrate solution under continuous stirring, and the homogeneous solution is neutralized with the addition of ammonium hydroxide (NH<sub>4</sub>OH). Following this, different amounts (0.1%, 0.2%, and 0.3%) of magnesium nitrate hexahydrate (0.3 M) were introduced into the aforementioned solution. Fourth stage (IV): the overall homogenous solution was evaporated using a heating system; it was kept on a hot plate at 100 °C with intensive stirring for about 1–2 hours. Thus, a highly viscous gel was obtained. Fifth

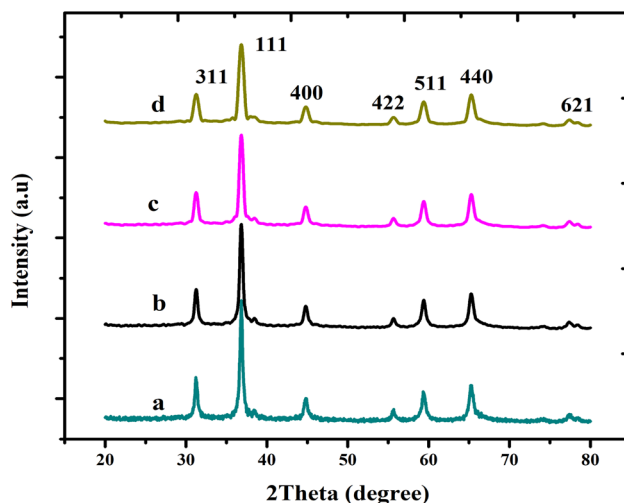
stage (V): the extremely viscous gel was then transferred to a muffle furnace, where self-ignition was initiated at an experimental temperature of 400 °C/5 hours. The samples (Table 1) of the (0.0) undoped CuCr<sub>2</sub>O<sub>4</sub> and (0.1 to 0.3) from Mg-doped CuCr<sub>2</sub>O<sub>4</sub> were labelled (a) and (b) to (d).

### 2.1. Instrumental

X-ray diffraction analysis was carried out using a Rigaku DMAX-3A powder diffractometer with CuK $\alpha$  radiation at a wavelength of 1.54 Å to investigate the crystalline phase and the various structural parameters of the prepared samples. These patterns of XRD were scanned in a 2 $\theta$  range of 20° to 80° with a scanning step size of 0.05°. The morphology was characterized *via* field-emission scanning electron microscopy (FESEM) (SEM, QUANTA FEG 250, USA) and transmission electron microscopy (TEM). The specific surface areas (BET) of the products were tested using a Micromeritics ASAP 2020 apparatus. Fourier-transform infrared (FTIR) spectra were recorded using a thermo scientific Nicolet iS10 instrument in an *in situ* Harrick IR cell.

### 2.2. Catalytic test

Catalytic oxidation of alcohol was carried out on a batch reactor functioning under atmospheric conditions. 10 mmol of (CH<sub>3</sub>CN, DMF and CHCl<sub>3</sub>), 10 mmol of veratryl alcohol (at a molar ratio of H<sub>2</sub>O<sub>2</sub>/alcohol of 1 : 1), and 10 mmol of oxidant (TBHP/H<sub>2</sub>O<sub>2</sub>) was added along with 0.1 to 0.3 g of the pure and Mg-doped copper chromites, and the fillings were heated to 100 °C at different reaction times for 12 h at altered time intervals in a three-necked round bottom flask equipped with a reflux condenser and the thermometer.

**Fig. 1** X-ray diffraction pattern of (a) CuCr<sub>2</sub>O<sub>4</sub> and (b–d) Mg-doped CuCr<sub>2</sub>O<sub>4</sub>.

Chromium nitrate 1 M solution, and copper nitrate 0.5M solution



Dissolved 25 ml (DI) deionized water/1.hrs.  
(Stirring continuously)

Together (Cr and Cu) get the homogenous solution + citrate towards nitrate ratio  
were fixed on the one



Homogeneous solution is reached on the for addition (NH<sub>4</sub>OH)



Magnesium nitrate hexahydrate, 0.3 M dopant concentration (0.1%, 0.2% and 0.3%)



Overall homogenous solution /heating system on the 100°C by stirring form about 1-2 hours



Highly viscous gel into 400°C/5hours



Pure and Mg doped samples

Flow chart of synthesis form pure and Mg doped copper chromites

From these values, the overall conversion of the reactant veratryl alcohol and the selectivity of the product (3) was estimated.

$$\text{Conversion (\%)} = \frac{V_{\text{veratryl alcohol}} - V_{\text{veratraldehyde}}}{V_{\text{veratryl alcohol}}} \times 100$$

$$\text{Selectivity (\%)} = \frac{V_{\text{veratraldehyde}}}{\text{Consumed}_{\text{veratryl alcohol}}} \times 100,$$

$$\text{Yield} = \frac{\text{moles product produced}}{\text{moles paraffin charged}} \times 100\%$$

0424), these XRD peaks conform to undoped and Mg-CuCr<sub>2</sub>O<sub>4</sub>, matching well with the standard. As the amount of Mg doping increased from  $x = 0$  to 0.1, 0.2, and 0.3%, the samples showed only copper chromite's phase, and the peak intensities were comparable with the pure CuCr<sub>2</sub>O<sub>4</sub> sample. This indicates the integrity of the Mg dopant within the copper chromite crystal structure. XRD patterns ranging from 35.5° to 37.5° were assigned to the 111 plane, which has the highest intensity. Furthermore, the primary peaks at  $2\theta$ -values adhering to the (111) and (311) planes show a small change as the doping concentration of Mg quantity increases. The XRD peaks of the

Table 2 Crystallite size, lattice parameters and lattice strain of copper chromite and Mg-doped copper chromates

Samples	Crystallite size (nm)	Lattice parameters		Strain
		$a = b$ (Å)	$c$ (Å)	
a	43.12	5.9832	3.9810	3.234
b	38.45	5.9833	3.9811	3.091
c	31.45	5.9835	3.9833	2.981
d	29.98	5.9837	3.9835	2.567

### 3. Results and discussion

#### 3.1. XRD pattern of the Mg-doped CuCr<sub>2</sub>O<sub>4</sub> nanocomposites

The XRD measurements were performed to determine the effectiveness of the production on the pure and Mg-doped CuCr<sub>2</sub>O<sub>4</sub>. As shown in Fig. 1, the obtained XRD peaks are indexed as undoped and Mg-CuCr<sub>2</sub>O<sub>4</sub> with a cubic structure formation. As confirmed by a standard card (JCPDS No. 34-



samples progressively changed between low and high angles, which correlated with the extension (Table 2) of the lattice parameters, cell volume ( $\text{\AA}^3$ ) and  $d$  spacing values. Thus, ionic radii of  $\text{Mg}^{2+} = 86$  pm,  $\text{Cr}^{3+} = 75.5$  pm, and  $\text{Cu}^{2+} = 77$  pm were compared. Mg-doped copper chromites have smaller crystallite sizes than pure copper chromites due to the substitution of the lattice ions by the  $\text{Mg}^{2+}$  ions and their entry into interstitial locations.<sup>15,16</sup>

The average crystallite size was determined using the Scherrer formula:<sup>17</sup>

$$L = \frac{0.89\lambda}{\beta \cos \theta}$$

where  $L$  is the mean crystal size ( $\text{\AA}$ ) and  $\lambda$  is the wavelength of the X-ray source ( $1.5404 \text{ \AA}$ ), thus, in the XRD pattern,  $\theta$  and  $\beta$  correspond to the (radians) diffraction angle of the observed peaks and the full width at half maximum (FWHM), respectively. 0.89 is the Scherrer constant. Thus, for peak position, FWHM can be acquired with two Gaussian curves by fitting the measured peaks. The monochromatic  $\text{Cu K}\alpha$  radiation was used as a X-ray source. Based on the results of X-ray diffraction, the decrease in crystallite size from (a) pure  $\text{CuCr}_2\text{O}_4$  43.12 nm, Mg-doped  $\text{CuCr}_2\text{O}_4$  samples (b–d) 38.45 nm, 31.45 to 29.98 nm could be linked to maximizing the concentrations of dopant.

### 3.2. FTIR spectra

Fourier transform infrared (FTIR) spectroscopy was recorded for the four undoped samples (Fig. 2a and b) and Mg- $\text{CuCr}_2\text{O}_4$  around room temperature from 400 to  $4000 \text{ cm}^{-1}$ . Thus, two sharp bands for the different absorption peaks observed around  $561$  and  $475 \text{ cm}^{-1}$  lower frequency band ( $\nu_2$ ) correspond to the vibration of  $-\text{Mg}^{2+}-\text{Cr}^{3+}-\text{O}^{2-}$  by sites, indicating the formation of octahedrons and tetrahedrons, respectively (Table 3). The bands around  $560$ – $470 \text{ cm}^{-1}$  correspond to the intrinsic stretching vibration of metal ions at the tetrahedral site, and the band in the range of  $510$ – $550 \text{ cm}^{-1}$  is attributed to the M–Mg–O

Table 3 FTIR modes ( $\nu_1$  and  $\nu_2$ ) of copper chromite and Mg-doped copper chromite

Samples	Wave number $\nu_1$ ( $\text{cm}^{-1}$ )	Wave number $\nu_2$ ( $\text{cm}^{-1}$ )
a	613, 801	898, 1125
b	608, 799	894, 1122
C	605, 796	890, 1120
D	661, 856	1118

bond vibration. These two bands positioned a high-frequency band ( $\nu_1$ ) at  $500$  and  $678 \text{ cm}^{-1}$  characteristic of  $\text{CuCr}_2\text{O}_4$  spinel. The FT-IR spectra exhibited two characteristic absorption bands at  $600$  and  $900 \text{ cm}^{-1}$ , corresponding to the tetrahedral and octahedral formations, respectively. Thus, both bands similarly correspond to the asymmetric stretching vibrations of Cr–O–Cu–Mg. In general, Mg substitution *via* transition metal ions, such as  $\text{Cu}^{2+}$ , leads to a shift in the frequency bands and is due to the variation of  $\text{CrO}_4$  bond length.<sup>18,19</sup>

### 3.3. Morphology

SEM images and micrographs of the undoped and Mg- $\text{CuCr}_2\text{O}_4$  compositions ( $x = 0.00, 0.1, 0.02$  and  $0.03\%$ ) are demonstrated in Fig. 3a–d. The SEM images and micrographs show irregularly shaped large grains of undoped and smaller grains of Mg- $\text{CuCr}_2\text{O}_4$ . In the arrangement within the SEM results, the samples have an extensive particle distribution and present strong agglomerations; hence, a measurement from the particle size was not possible. However, the obtained results give some statistical arrangements of Mg–Cu–Cr–O. As can be observed, SEM images detect particularly pure and doped sample differences between XRD crystallite sizes and particle sizes, as shown in Table 4. The crystallite size determined using the XRD approach was found to be correct, however the grain size assessed using the SEM analysis had broader values and may

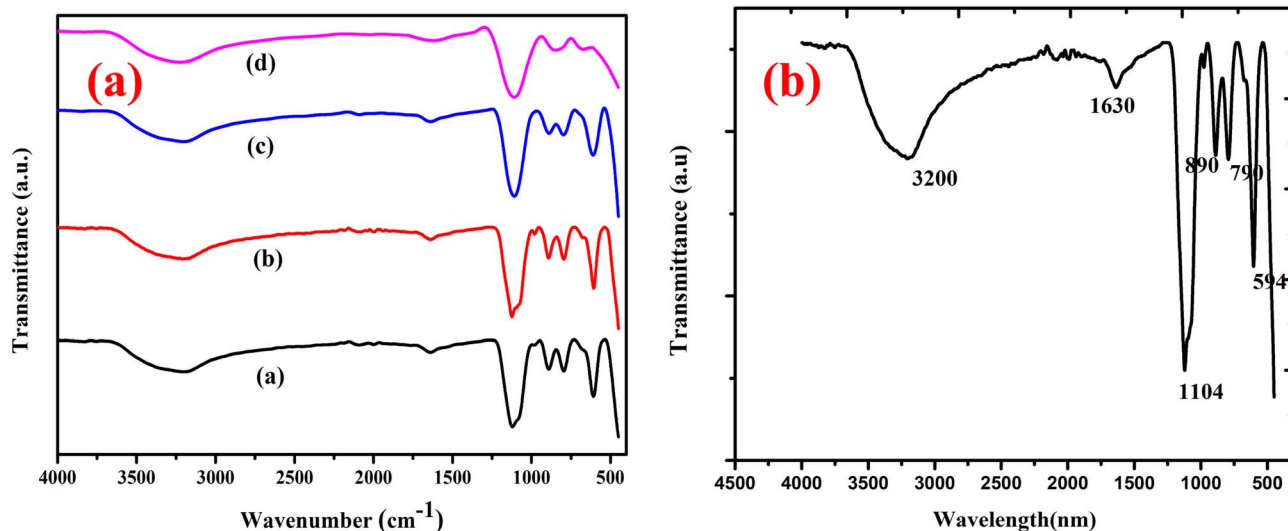


Fig. 2 (a) FTIR spectra of (a)  $\text{CuCr}_2\text{O}_4$  and (b–d) Mg-doped  $\text{CuCr}_2\text{O}_4$ ; (b) FTIR spectra of pure  $\text{CuCr}_2\text{O}_4$ .





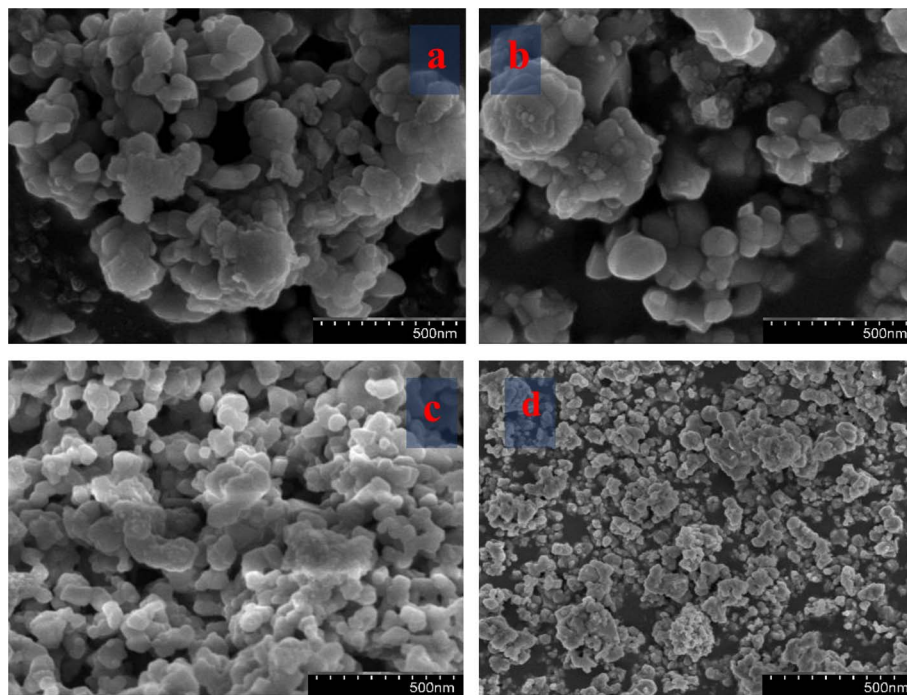


Fig. 3 SEM showing (a)  $\text{CuCr}_2\text{O}_4$  and (b–d) Mg-doped  $\text{CuCr}_2\text{O}_4$ .

**Table 4** Difference between the calculated crystallite sizes (XRD) of samples and the grain sizes (SEM) of copper chromite and Mg-doped copper chromites

Samples	Crystallite size from XRD (nm)	Particle size from SEM (nm)
a	43.12	49–53
b	38.45	43–39
c	31.45	40–31
D	29.98	39–29

have measurement errors. In our studies,  $\text{CuCr}_2\text{O}_4$  nanocomposites having a cluster-like structure with sizes ranging from 100 to 500 nm made by identical particles. Pure and doped samples both have discrete particle-like appropriate interfaces in  $\text{CuCr}_2\text{O}_4$  nanocomposites. In addition, it is noticed that the structure can be obtained at lower synthesis temperatures from the conventional method.<sup>20</sup> Thus, TEM was used to control the morphologies and particle size of copper chromite and the Mn doping copper chromite. As illustrated in Fig. 4a–d, spherical particles and regular structures are present in the doped samples. TEM images for  $\text{CuCr}_2\text{O}_4$  particles were obtained and the particle-like shape changed to form spherical particles, as concentration on the  $\text{Mg}^{2+}$  is improved.

### 3.4. Surface area analysis

Thus, a specific surface area can be used from the BET equation to determine the amount of nitrogen absorbed into copper chromite and the Mn doping copper chromite. The H–K method was used to obtain the average pore diameter, and the  $t$ -

plot method was employed to obtain the total pore volume. In terms of catalytic activity, surface area is an important parameter when evaluating potential catalytic applications involving catalytic materials such as copper chromite and Mg-doped copper chromite. Table 5 displays the pore volume ( $V_p$ ), specific surface area ( $S_{\text{BET}}$ ), pore radius ( $R_p$ ), and crystallite size (nm). The copper chromite and Mg-doped copper chromite samples increase the surface area for converted catalytic applications because they demonstrate increasing contact between alcohol reacting molecules and aldehyde from the active sites.<sup>21,22</sup> For all the samples, this was followed by the type III isotherms with the hysteresis loop at the high  $P/P_0$  and illuminating the representative mesoporous material.<sup>23</sup> The system, copper chromite and the Mg-doped copper chromite of the plot on the amount of gas adsorbed as a function of the relative pressure are exposed altogether as a type-III (a–d) and with hysteresis loop, as shown in Fig. 5a.

When magnesium is added, the bulk copper chromite phase grows more slowly, increasing the surface area, improving porosity, and creating micropores. Because of nonisomorphic substitution, the addition of magnesium to the copper chromite phase matrix causes a decrease in grain size, which results in an increase in surface area. The three components of Mg, Cr, and Cu can form pores in their matrices, leading to the production of pores of varying sizes. The reduction in grain size and the non-isomorphic substitution of Mg in the copper chromite matrix resulted in the formation of significant micropores, which is why the average pore diameter for the Mg-doped sample decreased. Thus, the addition of Mg, which simultaneously increases the mesopores and introduces micropores, increases the catalytic activity of copper chromites.<sup>24,25</sup>

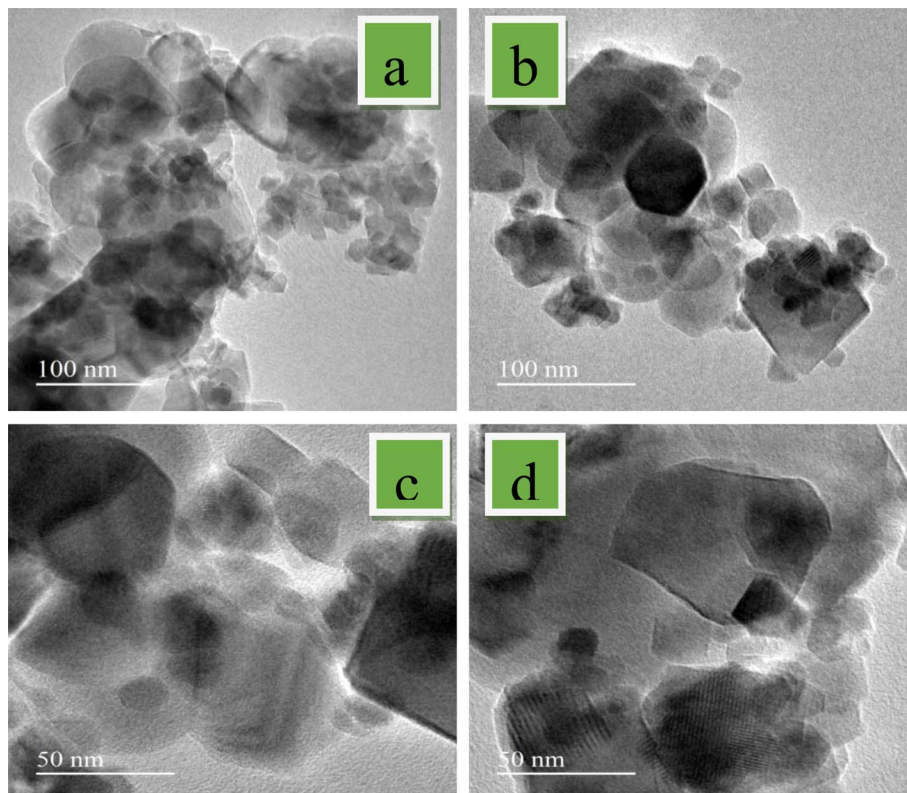


Fig. 4 TEM images of (a)  $\text{CuCr}_2\text{O}_4$  and (b–d) Mg-doped  $\text{CuCr}_2\text{O}_4$ .

Table 5 BET surface area, average pore diameter, pore volume and crystallite size (nm) of  $\text{CuCr}_2\text{O}_4$  and Mg-doped  $\text{CuCr}_2\text{O}_4$

Parameters	a	b	c	d
$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	38.2	40.2	57.8	63.4
$S_{\text{mic}}$ ( $\text{m}^2 \text{g}^{-1}$ )	2.9	5.1	7.5	9.2
$S_{\text{meso}}$ ( $\text{m}^2 \text{g}^{-1}$ )	35.3	35.1	50.0	54.1
Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.1	0.1	0.1	0.2
Micro pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.0	0.0	0.1	0.1
Meso pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.1	0.1	0.0	0.1
Average pore diameter (nm)	13.6	14.1	17.9	19.8

## 4. Catalytic activity of selective oxidation

### 4.1. Effect of temperatures

The effect of temperature on selectivity towards veratryl aldehyde and the conversion of veratryl alcohol were studied in the range of 60–140 °C, as presented in Fig. 6. The selectivity (80%) of veratryl aldehyde decreases with increasing temperature, which is particularly due to the over-oxidation of veratryl aldehyde to veratric acid. However, conversion of veratryl alcohol increased from 60 to 80% with an increase in the temperature from 60 to 140 °C.<sup>26–28</sup> This system increased the reaction temperature, which was important for the decrease in the oxygen, resulting in unfavorable product formation. The optimum temperature is 100 °C.

### 4.2. Amount of catalyst

The effect of catalyst amount (0.1 g to 0.5 g) on the selectivity of veratryl aldehyde and the conversion of veratryl alcohol into by-products formation were studied and the results are presented in Fig. 7. The catalytic activity is closely related to the following two factors: the copper chromite amount of catalyst for the active sites Cu and Cr and the size for  $\text{O}^{2-}$ . The doping concentration of Mg was determined to ensure appropriate active Mg sites; however, smaller Mg particles are usually obtained. Therefore, the optimal pure and doping copper chromites are 0.3 g because they give the best yield among others. However, the amount of catalyst interaction with the catalyst regenerates the catalyst surface, causing the product molecules to desorb and encouraging additional oxidation.

### 4.3. Effect of reaction time

This conversion of veratryl alcohol and the selective formation of product are observed at different reaction time intervals of 0.5, 1, 2, 4, 6, 8, 10, 12 and 14 h. As demonstrated in Fig. 8, 11% veratryl alcohol conversion and 50% veratryl aldehyde selectivity are obtained at 0.5 h; after allowing the reaction for 10 h, 80% yields were formed. The main product was veratryl aldehyde with veratryl acid as a by-product. Based on the catalytic reaction route, to increase the conversion of aldehyde, the reaction time needs to be prolonged. Thus, the catalytic activity was achieved with a reaction time of 12 h and a high yield was obtained, and the time was increased as the products formed.<sup>29</sup> Thus, an optimum catalytic reaction time of 12 h was selected.



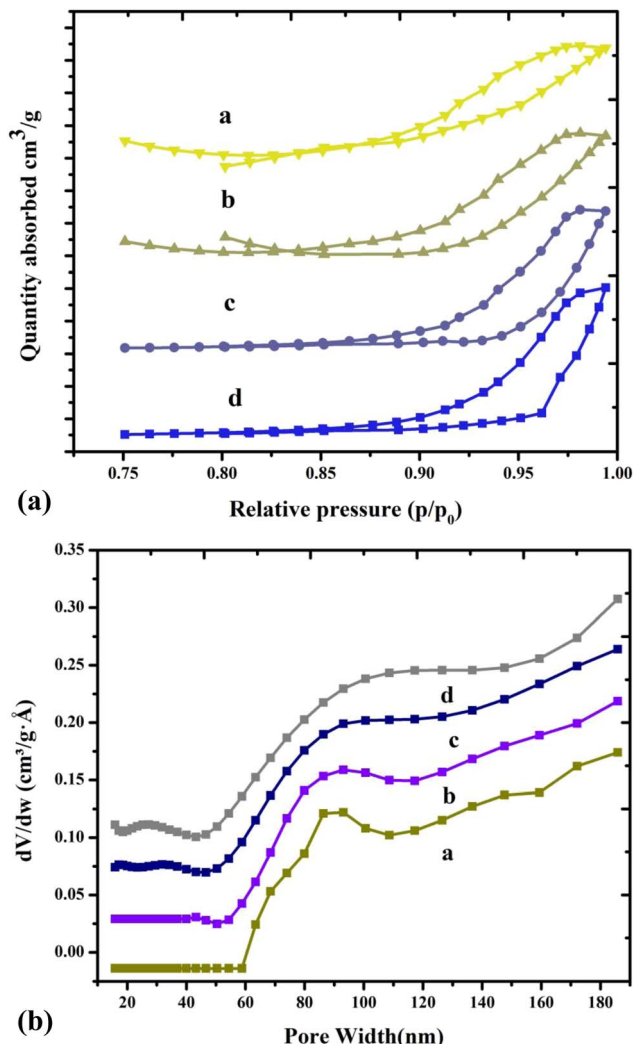


Fig. 5 (a) N<sub>2</sub> adsorption/desorption isotherms of (a) pure and (b–d) Mg-doped copper chromite. (b) Pore size distributions of (a) pure and (b–d) Mg-doped copper chromites.

#### 4.4. Effect of solvents

The catalytic performance was evaluated in several solvents, such as chloroform (CHCl<sub>3</sub>), acetonitrile (CH<sub>3</sub>CN) and dimethyl formamide (DMF), for the conversion of veratryl alcohol to veratryl aldehyde. Thus, a solvent plays an important role in the reaction induced by the alcohol conversion of an aldehyde decomposed for the by-products. Consequently, a higher yield for acetonitrile than for dimethyl formamide and chloroform was observed, as listed in Table 6. For this reason, a polar solvent was more easily adsorbed on the catalyst surface, preventing the adsorption of alcohol to aldehyde. Because the substrates and oxidants are more soluble in the solvent, they can more readily bind to the catalyst's active sites. Therefore, acetonitrile was the more active solvent for the catalytic system under study. In the case of CHCl<sub>3</sub> and DMF, the yields are lower compared to acetonitrile, might be due to the inefficient hydrogen transfer by solvents, and the incomplete solubility of organic substrates and catalytic systems in the solvents. It turned out that the conversion of alcohol depended on the

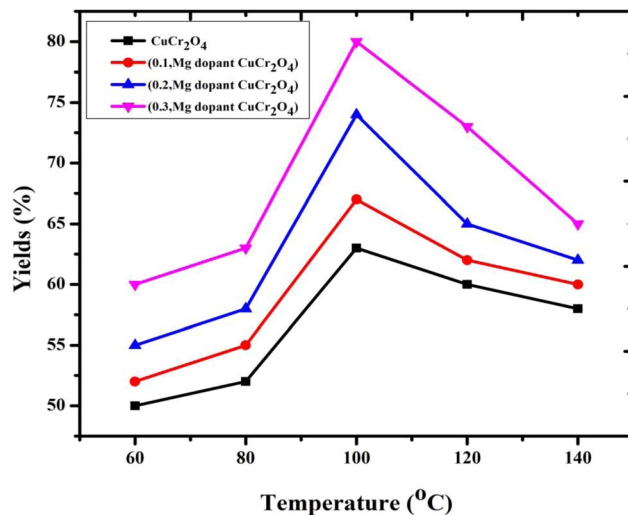


Fig. 6 Catalytic activity of the catalysts versus different reaction temperatures in the oxidation of veratryl alcohol. Reaction conditions: pure and doped samples: 0.3 g; alcohol: 10 mmol; acetonitrile: 10 mmol; H<sub>2</sub>O<sub>2</sub>: 10 mmol; time: 12 h; temperature: 60 to 140 °C.

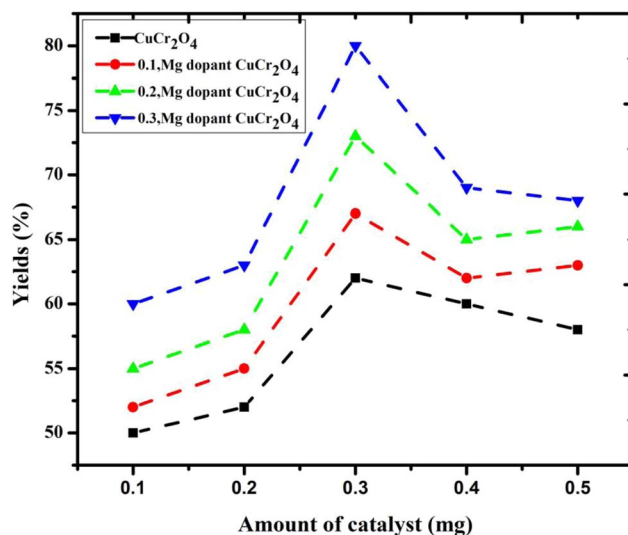


Fig. 7 Yield of the product via the selective oxidation of veratryl alcohol using different catalysts. Reaction conditions: pure and doped samples: 0.1 to 0.5 g; alcohol: 10 mmol; acetonitrile: 10 mmol; H<sub>2</sub>O<sub>2</sub>: 10 mmol; time: 12 h; temperature: 100 °C.

polarity of the solvent molecules, polarity order from acetonitrile, dimethyl formamide and chloroform. Besides, acetonitrile was selected as the solvent for the catalytic system.

#### 4.5. Effect of oxidants

Catalytic performance for oxidation as a function of the oxidant played an important role. This catalytic reaction is controlled by the option for the reaction to occur due to the contribution of the oxygen lattice (Fig. 9) from the oxidant. Hereafter, the reaction was successively carried out in the presence of different oxidants, such as TBHP and hydrogen peroxide. TBHP was slightly soluble on the selected organic substrate and the



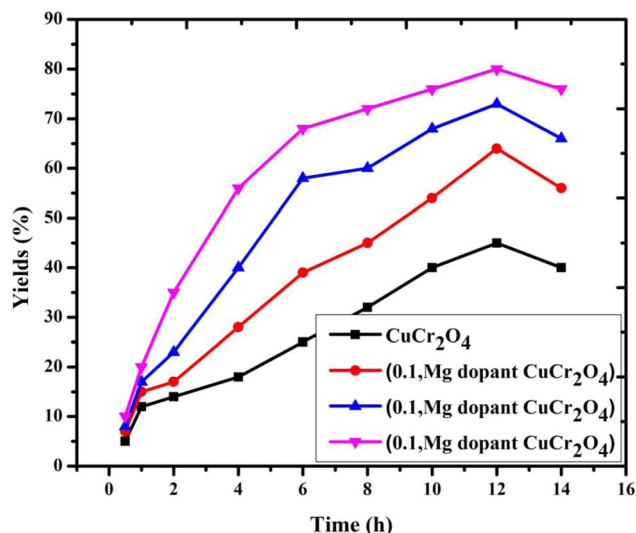


Fig. 8 Catalytic activity of the catalysts *versus* different reaction times for the selective oxidation of veratryl alcohol. Reaction conditions: pure and doped samples: 0.3 g; alcohol: 10 mmol; acetonitrile: 10 mmol;  $\text{H}_2\text{O}_2$ : 10 mmol; time: 0 to 16 h; temperature: 100 °C.

Table 6 Yield of the product in different oxidants obtained via veratryl alcohol<sup>a</sup>

Samples	Chloroform	Dimethyl formamide	Acetonitrile
a	32	40	46
b	45	54	65
c	59	67	78
d	68	73	83

<sup>a</sup> Reaction conditions: pure and doped samples: 0.3 g; alcohol: 10 mmol; acetonitrile:  $\text{CHCl}_3$  and DMF 10 mmol;  $\text{H}_2\text{O}_2$ : 10 mmol; time 12 h; temperature: 100 °C.

catalytic system. As a result, the yield of veratryl aldehyde is low in all synthesized  $\text{CuCr}_2\text{O}_4$  nanomaterials. In the case of  $\text{H}_2\text{O}_2$ , the solubility on the chosen organic substrate could be higher. In conclusion,  $\text{H}_2\text{O}_2$  on acetonitrile was usual because the establishment of the peroxycarboximidic acid was intermediate and the transfer agent was good oxygen. Hence, the choice of the oxidant was hydrogen peroxide.<sup>30,31</sup>

#### 4.6. Mechanism

A proposed mechanism in Scheme 1 suggests that  $\text{H}_2\text{O}_2$  molecules undergo homolytic cleavage, resulting in two hydroperoxy radicals. These radicals react with  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  ions on the surface of  $\text{CuCr}_2\text{O}_4$ , creating  $\text{Cr}^{2+}$  and  $\text{Cu}^+$  ions and regenerating hydroperoxyl. The hydroperoxy radicals also react with hydroxy radicals on the surface to form water and oxygen. Veratryl alcohol molecules are adsorbed onto the surface of  $\text{CuCr}_2\text{O}_4$ , forming metal-alkoxide intermediates and adsorbing hydrogen *via* O–H bond cleavage. The surface O–H group is formed by bonding adsorbed hydrogen with the surface lattice oxygen and coordinating with the carbon atom of the methyl group in the veratryl alcohol molecule. Finally, the C–H bond in the

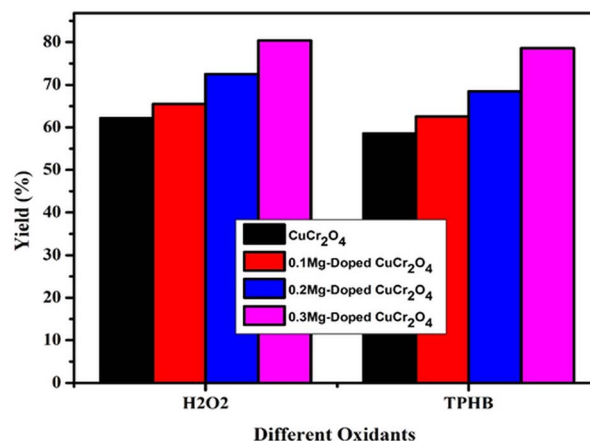
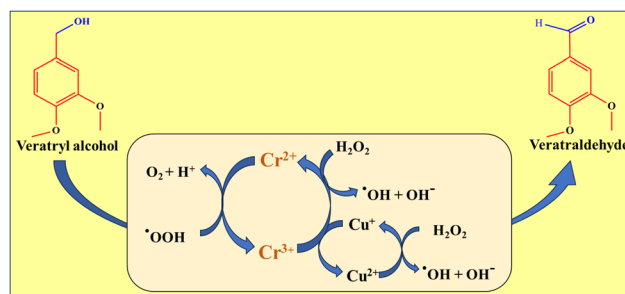
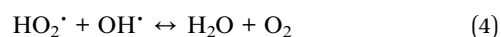
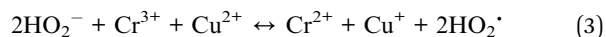
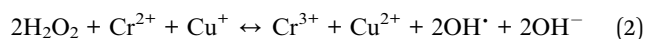
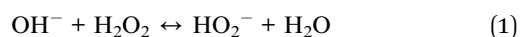


Fig. 9 Effect of oxidants in the selective oxidation of veratryl alcohol. Reaction conditions: pure and doped samples: 0.3 g; alcohol: 10 mmol; acetonitrile: 10 mmol; TBHP and  $\text{H}_2\text{O}_2$ : 10 mmol; time: 12 h; temperature: 100 °C.



Scheme 1 Shows the selective oxidation of veratryl alcohol to veratraldehyde.

$\beta$  position is activated, resulting in the formation of veratraldehyde and water. The oxygen adsorbed onto the support surface dissociates into chemisorbed oxygen species and diffuses into the lattice vacancies of the support. This is followed by activation in the oxygen vacancies and conversion into lattice oxygen ( $\text{O}^{2-}$ ). The lattice oxygen further transfers to the surface of  $\text{CuCr}_2\text{O}_4$  through oxygen-deficient sites, restoring the interface between the  $\text{CuCr}_2\text{O}_4$  active sites.<sup>32–35</sup>



#### 4.7. Recyclability of the catalyst

To examine the recyclability of the catalyst, the oxidation of veratryl alcohol to veratraldehyde was repeated five times with the same catalyst. The percentage conversion of veratraldehyde slightly decreased. The catalysts after the reaction were recovered by centrifugation, washed with ethanol, and then dried and





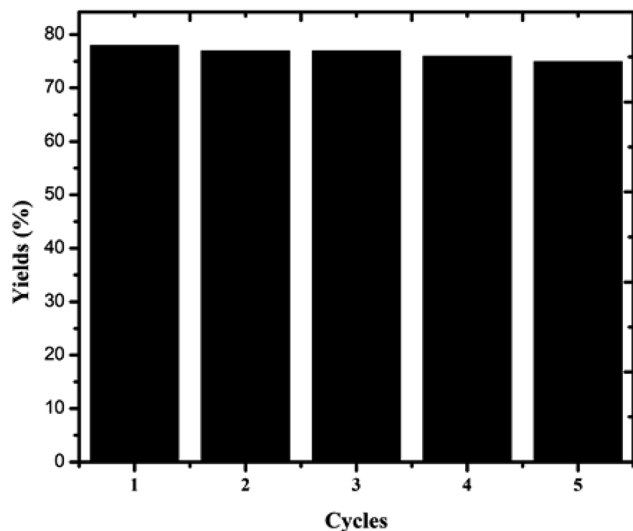


Fig. 10 Cycling performance of the copper chromite catalysts.

reused for another reaction under the same conditions, as shown in Fig. 10. From this determination, the samples were filtered and the residue was washed several times with acetone and dried at 120 °C in an air oven for 3 h; this was repeated five times under identical catalytic conditions. Consequently, considering the small amount of catalyst used in the reaction, the great loss of catalyst should be due to the process of washing, which could be easily addressed in the large scale industrial production.

During the catalytic oxidation of veratryl alcohol to veratraldehyde, O–H bonds are broken and attended through the formation of hydrogen atoms, which further react with oxygen to generate water to achieve dehydrogenation to produce veratraldehyde. Subsequently, one hydrogen atom in the CHO groups was formed *via* a broken O–H bond, forming a metal–alcohol salt intermediate. Further, the objectivity of the hydrogen atom from carbon induces the conversion of the alcohol group into an aldehyde.

## 5. Conclusions

This paper demonstrates a simple method for producing efficient catalysts for the catalytic oxidation of veratryl alcohol to veratraldehyde. The further detachment of a hydrogen atom from carbon causes the alcohol group to be converted into an aldehyde group, resulting in the creation of an intermediate and veratric acid. XRD confirmed the development of the spinel phase. Thus, pure and Mg-doped spinels were found to be highly porous, as confirmed by SEM. Thus, copper chromite nanocomposites with a crystallite size in the range of 43–29 nm were synthesized. FT-IR was used to confirm the formation of the spinel phase. The current technology is applicable to various d and f block metal-supported catalysts for further catalytic processes.

## Conflicts of interest

There are no conflicts to declare.

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