

## Spinel ferrites as efficient magnetically reusable nanocatalysts in the solvent-free synthesis of substituted trisphenols

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### ABSTRACT

A series of copper and cobalt substituted nanospinel ferrites have been synthesized by the hydrothermal method. These compounds were characterized by FT-IR, XRD, EDX, SEM and VSM techniques. All of the synthesized nanospinel ferrites were found to be highly efficient and magnetically recoverable in the solvent-free synthesis of substituted 2,6-(2-hydroxybenzyl)-phenols (trisphenols). A wide range of trisphenols were successfully synthesized from the reaction of 2,6-bis (methylol) phenols (BMPs) and different substituted phenols in the presence of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  nanocatalyst. The best results were obtained in the presence of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  and molar ratios of phenol: BMP: catalyst, 3: 1: 0.1 under solvent-free conditions at  $90^\circ\text{C}$ . The catalyst could be easily separated using an external magnet. Comparison of the efficiency of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  with other reported catalytic systems showed that this catalyst has a higher activity for the synthesis of trisphenols. All the products were obtained in short reaction times and high yields. This could be related to the synergistic catalytic effect of copper and cobalt in the nanospinel on the activation of hydroxyl groups of BMPs.

**Keywords:** Spinel ferrites, Magnetic nanocatalyst, Synergistic catalytic effect, Trisphenols, Antioxidant.

### 1. Introduction

Recently, polyphenolic compounds have attracted increasing interest because of their special industrial, pharmaceutical and biological activities. These compounds have been used as drugs [1-5], antioxidants, photoresist materials and in the synthesis of important organic compounds such as calixarenes and crown ethers [6,7]. The multipresence of hydroxyl groups in the structure of these compounds led to their antioxidant performance. Moshfegh and his coworkers reported that the presence of halogen atoms in the structure of trisphenols, enhances their biological activity [8,9].

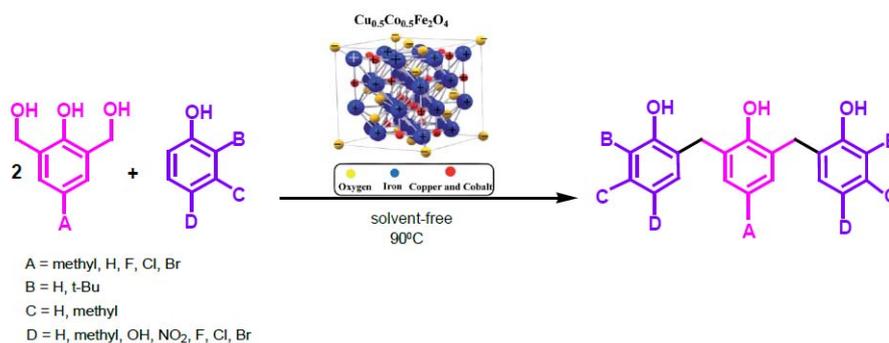
Despite the wide applications of trisphenolic compounds in various industries, only a few methods have been reported for the synthesis of these materials. Each of these methods has its benefits; nevertheless, they suffer from disadvantages such as low yield of the products, long reaction times, use of mineral and corrosive acid catalysts, use of large excess phenol and toxic solvents [8-13].

So, there is much room left to develop more efficient catalytic systems for the synthesis of trisphenolic compounds.

Recently, magnetic nanoparticles (MNPs) have gained increasing interest as catalysts due to their high performance, easy preparation from inexpensive and available precursors and simple mode recovering by implying an external magnet [14-17]. One of the most important classes of MNPs is spinel ferrites ( $\text{MFe}_2\text{O}_4$ ). These compounds have been widely used in gas sensors [18], adsorption [19], electrodes [20], MRI contrast agents [21] and catalysts [22,23]. Considering the existence of two or three metals in the structure of spinel ferrites, it can open up an efficient catalytic system. It is due to a synergistic catalytic effect of these metals [24-35].

Due to the aforementioned wide range of applications of trisphenols and in continuation of our work towards the development of new catalytic systems for simple and efficient synthesis of phenolic antioxidants [10, 36-39], here in we report a simple, efficient and solvent-free method for the synthesis of trisphenols using nanospinel ferrites ( $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $0 \leq x \leq 1$ )) as magnetically reusable catalysts (Scheme 1).

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**Scheme 1.** Synthesis of 2,6-bis-(2-hydroxy benzyl)-phenol derivatives in the presence of nanospinel ferrites.

## 2. Experimental

Chemicals were purchased from Sigma and Merck chemical companies. Melting points were determined using an IA 8103 melting point apparatus. <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) solvent using a DRX-300 spectrometer at 300 and 75 MHz, respectively, and trimethylsilane (TMS) as an internal standard. Elemental analysis for C, H, and N were performed using a Heraeus CHN rapid analyzer. VSM test was performed using a homemade instrument (Meghnatis Daghigh Kavir Company, Iran).

### 2.1. Synthesis of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles

$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles were prepared according to our previous report using a hydrothermal method [22]. In a typical procedure, 1.0 g CTAB was dissolved in 35 mL of deionized water. Then, 1.0 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was added to it and the mixture was stirred for 10 min. In the next step, 0.16 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.22 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  salts were dissolved in deionized water and added into iron solution with a burette. An aqueous solution of NaOH (5 M) was introduced drop-wise (pH= 10–11) and the mixture was stirred for 30 min again. The resultant materials were transferred into an autoclave (L= 7.3 cm, D= 3.9 cm). The autoclave was kept at 160°C for 72 h. After three days, the autoclave was allowed to cool down slowly to room temperature. The material was washed several times with deionized water and dried at room temperature. Then it was calcined at 750°C for 5h.

### 2.2. General Procedure for the synthesis of 2,6-(2-hydroxybenzyl) phenol derivatives (Trisphenols)

In a 25 mL round bottom flask, a mixture of BMP (1 mmol), substituted phenol (3 mmol) and  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  (0.1 mmol) was heated at 90°C and stirred until TLC monitoring indicated no further progress. Subsequently, the reaction mixture was

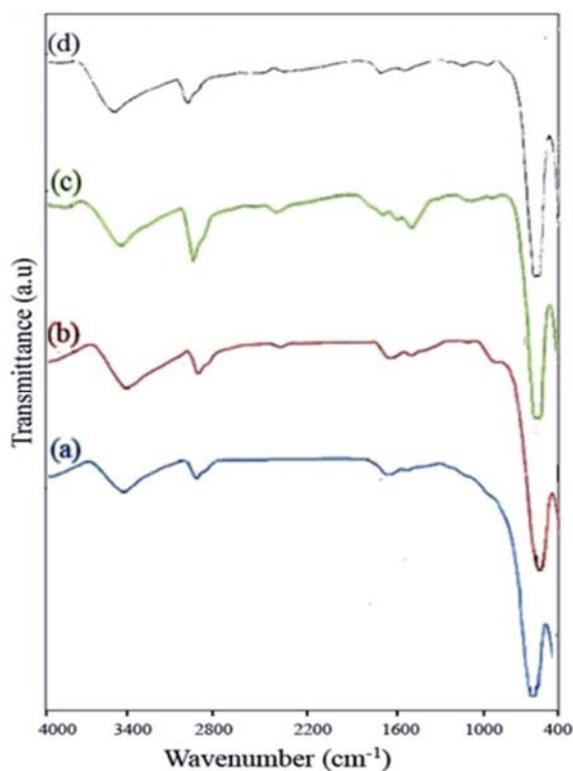
cooled to r.t. and 5 mL acetonitrile was added. The catalyst was separated using an external magnet. Organic phase was concentrated under reduced pressure. Finally, the product was purified by column chromatography (n-hexane/ ethyl acetate as eluent).

## 3. Result and Discussion

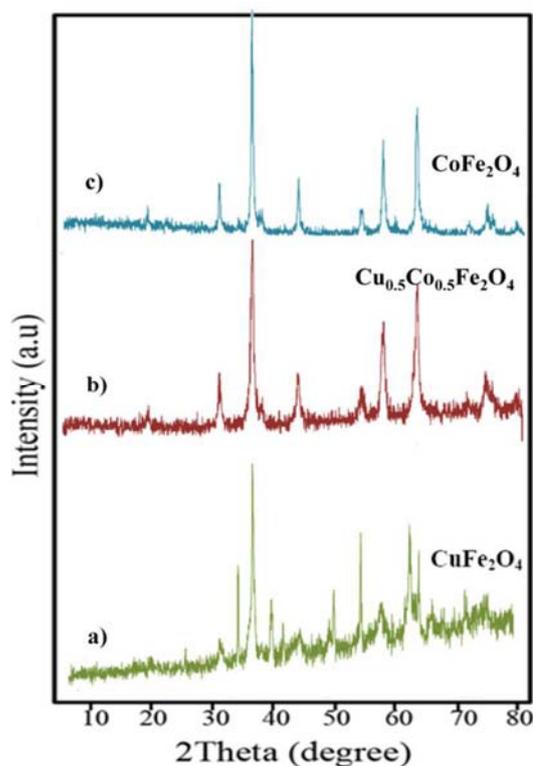
Cobalt-Copper magnetic nanospinel ferrites ( $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ) with various Co and Cu percent were prepared and characterized according to our previous report using a hydrothermal method [22]. A brief description of these characterizations is presented here. In the FT-IR spectra of these nanospinel ferrites (Fig. 1), two important broad bands observed in the range of 550-600  $\text{cm}^{-1}$  and 385-400  $\text{cm}^{-1}$  correspond to the vibration of metal-oxygen bond at tetrahedral and octahedral sites, respectively. X-ray diffraction pattern confirmed the phase purity and cubic spinel structure of the prepared mixed ferrites (Fig. 2). Based on the XRD peaks and Debye-Scherrer equation, the crystalline sizes of  $\text{CuFe}_2\text{O}_4$ ,  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  were estimated to be 18, 22 and 20 nm, respectively. Also, SEM images (Fig. 3) showed the grain sizes of 48, 34, 24, 24 and 29 nm for  $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  when x is 0, 0.25, 0.5, 0.75 and 1 respectively, which are in good agreement with XRD data.

EDX was also used for further clarifying the existence of metals and getting information about the chemical composition of the two synthesized nanospinel ferrites (Fig. 4 and Table 1). EDX spectrum demonstrates 0.5 of Cu and 0.5 of Co for  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  (Fig. 4a). This spectrum also shows the existence of the other elements such as Fe and O in the structure of this spinel. As shown in Fig. 4b, there is no evidence for the existence of Cu in the spectrum of  $\text{CoFe}_2\text{O}_4$ .

To obtain a characterization data about the magnetic properties of the prepared nanospinel ferrites,  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  was subjected to vibration sample magnetometer (VSM).



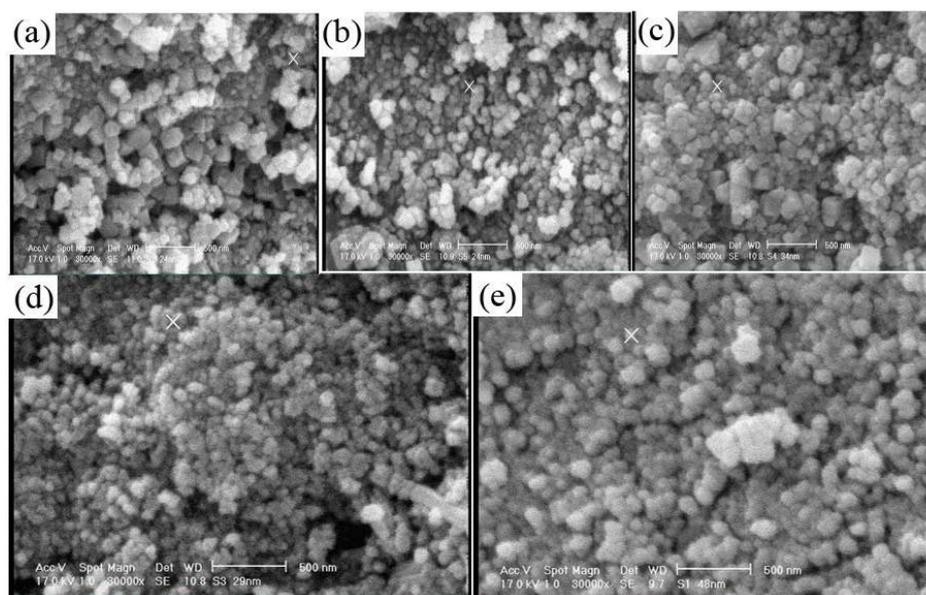
**Fig. 1.** FT-IR spectra of (a) CuFe<sub>2</sub>O<sub>4</sub> (b) Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> (c) Cu<sub>0.25</sub>Co<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> (d) CoFe<sub>2</sub>O<sub>4</sub>.



**Fig. 2.** XRD patterns of (a) CuFe<sub>2</sub>O<sub>4</sub> (b) Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> (c) CoFe<sub>2</sub>O<sub>4</sub>.

The VSM curve of this sample is shown in Fig. 5. As can be seen in Fig. 5, this catalyst showed a hysteric behavior typical of ferrimagnetism with relatively high coercivity [40]. Also a high saturation magnetization (42 emu/g) was observed for the prepared catalyst. These characteristics provide

a versatile confirmation to the fact that Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles could be completely separated from the reaction mixture using an external magnet and at the same time it could be dispersed in the reaction medium in the absence of magnetic field.



**Fig. 3.** SEM images of (a) Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> (b) Cu<sub>0.25</sub>Co<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> (c) Cu<sub>0.75</sub>Co<sub>0.25</sub>Fe<sub>2</sub>O<sub>4</sub> (d) CoFe<sub>2</sub>O<sub>4</sub> (e) CuFe<sub>2</sub>O<sub>4</sub>.

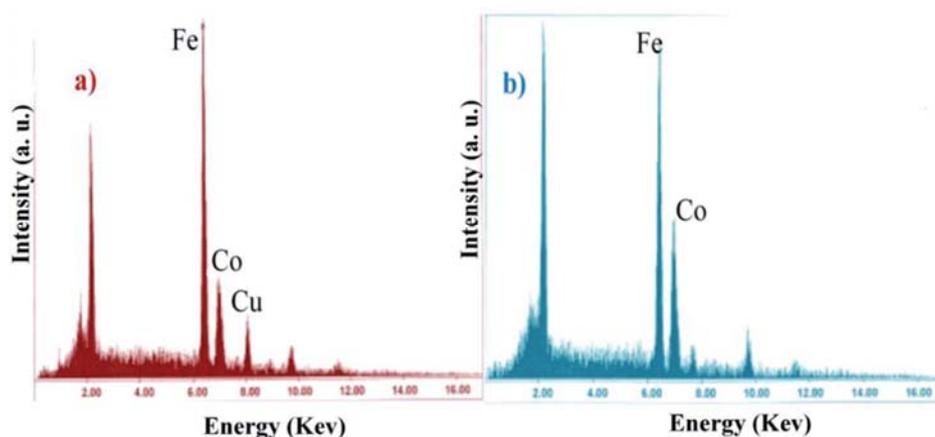


Fig. 4. EDX of (a)  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4$ .

After characterization of the synthesized magnetic nanospinel ferrites, the catalytic activities of them were evaluated in the synthesis of substituted trisphenols. Initially, the reaction of 4-chloro-2,6-(hydroxymethyl)-phenol (**5b**) and p-bromophenol (**7a**) was chosen as a model reaction to find the optimum conditions for the preparation of 2,6-bis-(5-bromo-2-hydroxybenzyl)-4-chloro-phenol (**15c**). The results of this study are summarized in Table 2.

It was found that, when the reaction was carried out without the catalyst, no desired product was obtained even after 2 h (Table 2, entry 15). Additionally, using  $\text{CuFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  as the catalyst in the reaction, resulted in 76 and 79% yield of the product, respectively (Table 2, entries 1, 5); which are much lower than when we used mixed spinels of copper and cobalt ( $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ) for this reaction (Table 2, entries 2, 3, 4). So, we can conclude that both Cu and Co play an important role in the reaction process. On the other hand, the copper and cobalt synergy increase the catalytic efficiency of the system. After that, the effect of various parameters such as solvent, temperature and molar ratios of the reactants and the catalyst on the model reaction were explored. Finally, we found that the best result is obtained in the presence of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  and molar ratios of phenol: BMP: catalyst, 3: 1: 0.1 under solvent-free conditions at  $90^\circ\text{C}$  (Table 2, entry 3).

**Table 1.** The EDX analysis results of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ .

Entry	Catalyst	Fe wt%	Co wt%	Cu wt%
1	$\text{CoFe}_2\text{O}_4$	65.70	34.30	0.00
2	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	63.49	18.26	18.25

To investigate the generality and the scope of this method, the optimized reaction conditions were extended to various BMPs as well as different substituted phenols (Table 3). Table 3 depicts that  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  is an effective catalyst for the synthesis of trisphenols. As can be seen from Table 3, all of the reactions proceeded efficiently. It should be noted that the effect of the nature of the substituents on the aromatic rings showed no obvious effect on these reactions; all of the products were obtained in short reaction times and high yields. This could be related to the synergistic catalytic effect of copper and cobalt in the nanospinel on the activation of hydroxyl groups of BMPs. The selectivity of this method was examined using 3,4-dimethylphenol as an asymmetric phenol with two ortho sites adjacent to OH group. In this case, the less hindered site was selectively alkylated (Table 3, entry 2).

Reusability of catalysts is an important subject from economic and environmental points of view. Therefore, the recyclability and reusability of the catalyst ( $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ) were tested for these reactions. It was done by separating it from the reaction mixture using an external magnet, decanting the solution and washing twice with acetonitrile. Finally, the catalyst was dried in an oven at  $100^\circ\text{C}$  for 2 h and reused in the next run. The results of this test are shown that the recovered catalyst could be reused for at least 7 runs (Yields were 92, 92, 90, 89, 88, 85 and 82, respectively) without a significant loss of its activity.

Comparison of the efficiency of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  with other catalytic systems in the synthesis of 2,6-bis-(5-bromo-2-hydroxy-benzyl)-4-chlorophenol is presented in Table 4. As Table 4 shows,  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  has a higher activity for the synthesis of this compound.

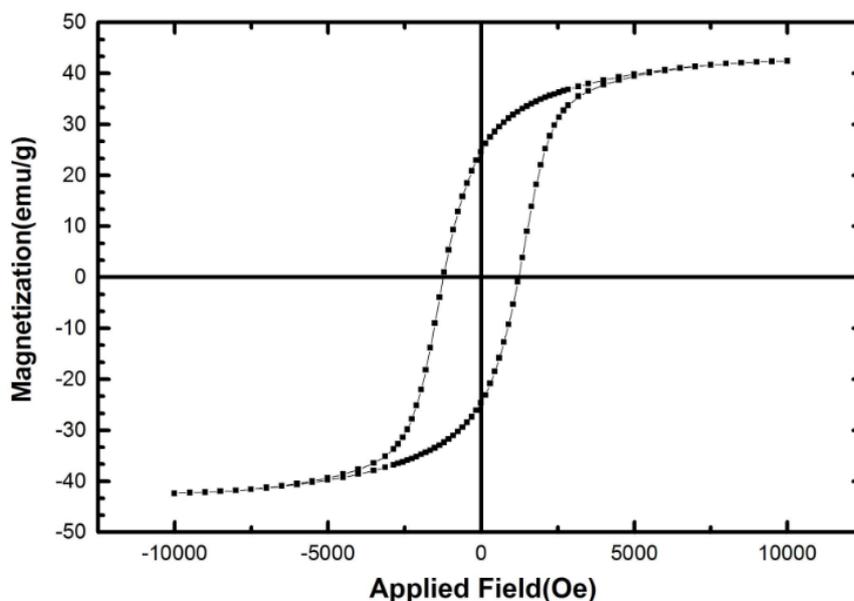
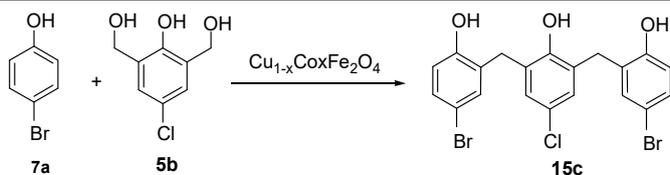


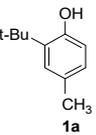
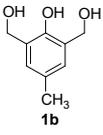
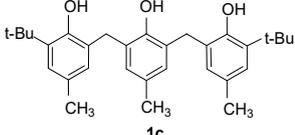
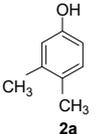
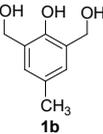
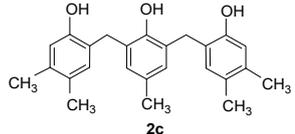
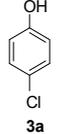
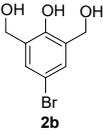
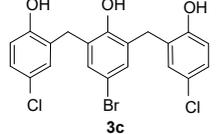
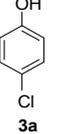
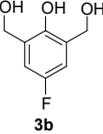
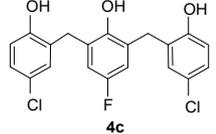
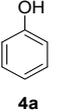
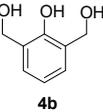
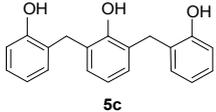
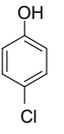
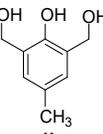
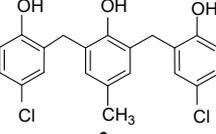
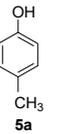
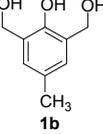
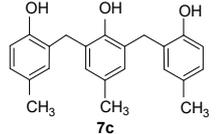
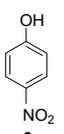
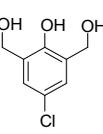
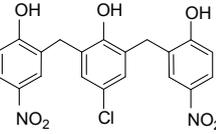
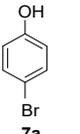
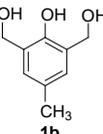
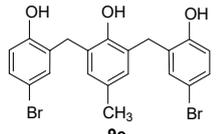
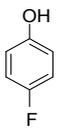
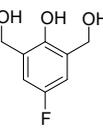
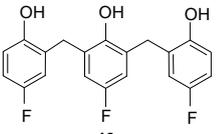
Fig. 5. VSM curve of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  magnetic nanoparticles.

Table 2. Optimization of the reaction conditions.

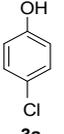
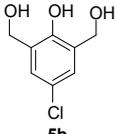
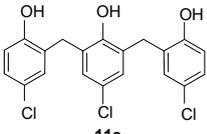
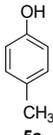
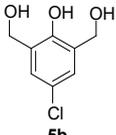
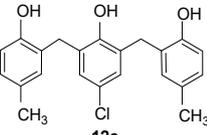
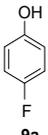
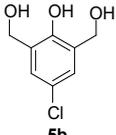
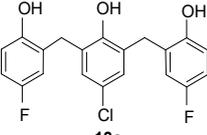
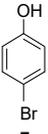
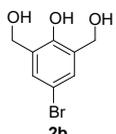
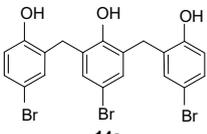
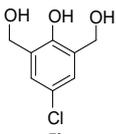
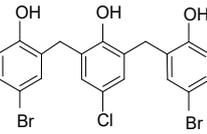
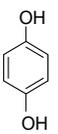
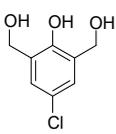
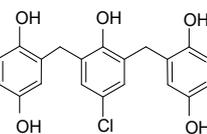


Entry	Catalyst	Solvent	Molar Ratios of Phenol/BMP/Catalyst	Temp. (°C)	Time (min)	Yield (%)
1	$\text{CuFe}_2\text{O}_4$	Solvent-free	3/1/0.1	90	30	76
2	$\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.1	90	15	84
3	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.1	90	15	92
4	$\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.1	90	20	86
5	$\text{CoFe}_2\text{O}_4$	Solvent-free	3/1/0.1	90	30	79
6	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Acetonitrile	3/1/0.1	Reflux	120	41
7	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	n-Hexane	3/1/0.1	Reflux	120	24
8	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	$\text{H}_2\text{O}$	3/1/0.1	Reflux	120	Trace
9	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	EtOH	3/1/0.1	Reflux	120	61
10	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	2/1/0.1	90	60	89
11	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	4/1/0.1	90	15	88
12	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.2	90	20	92
13	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.3	90	20	84
14	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.05	90	30	72
15	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.0	90	120	-
16	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.1	100	15	90
17	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	Solvent-free	3/1/0.1	80	30	86

**Table 3.** Synthesis of trisphenol derivatives.

Entry	<i>x</i> -Phenol	BMP	Trisphenol	Time (min)	Yield (%) <sup>a</sup>	m.p. (°C)		Ref.
						Found	Reported	
1	 <b>1a</b>	 <b>1b</b>	 <b>1c</b>	30	85	171-172	170-172	[34]
2	 <b>2a</b>	 <b>1b</b>	 <b>2c</b>	20	90	198-199	198-200	[34]
3	 <b>3a</b>	 <b>2b</b>	 <b>3c</b>	30	91	235-236	234-236	[34]
4	 <b>3a</b>	 <b>3b</b>	 <b>4c</b>	15	91	207-208	205-207	[34]
5	 <b>4a</b>	 <b>4b</b>	 <b>5c</b>	20	92	158-159	160-161	[36]
6	 <b>3a</b>	 <b>1b</b>	 <b>6c</b>	35	89	236-237	235-237	[36]
7	 <b>5a</b>	 <b>1b</b>	 <b>7c</b>	15	86	214-215	215-217	[36]
8	 <b>6a</b>	 <b>5b</b>	 <b>8c</b>	30	85	224-225	221-223	[10]
9	 <b>7a</b>	 <b>1b</b>	 <b>9c</b>	30	91	256-257	257-259	[34]
10	 <b>9a</b>	 <b>3b</b>	 <b>10c</b>	25	88	217-218	216-218	[34]

**Table 3.** (Continued)

11	 3a	 5b	 11c	25	92	221-222	233-235	[10]
12	 5a	 5b	 12c	15	93	135-136	137-139	[10]
13	 9a	 5b	 13c	35	88	221-222	223-224	[10]
14	 7a	 2b	 14c	30	87	236-237	236-238	[36]
15	 7a	 5b	 15c	15	92	250-251	251-253	[10]
16	 10a	 5b	 16c	15	91	179-180	178-180	[36]

<sup>a</sup>Isolated yield.**Table 4.** Comparison the efficiency of various catalysts in the condensation reaction of 4-chloro-2,6-bis-(hydroxymethyl) phenol and 4-bromophenol.

Entry	Catalytic System	Solvent	Time	Yield (%)	Ref.
1	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Solvent-free	15 min	92	This study
2	HCl	Methanol	12 h	68	[9]
3	ZnCl <sub>2</sub> / Microwave	Solvent-free	42 s	90	[11]
4	Silica sulfuric acid	1,4-Dioxane	1.5 h	85	[12]
5	Tungstosilicic acid	H <sub>2</sub> O	6 h	85	[10]
6	Nanosilica supported ionic liquid	Solvent-free	5 min	90	[34]

#### 4. Conclusion

In conclusion, Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> magnetic nanospinel ferrite was prepared, characterized and used as a highly efficient and reusable catalyst for the solvent-free synthesis of trisphenols. This catalyst was prepared using a simple procedure from commercially available

materials. A wide range of trisphenols were synthesized in high yields and short reaction times. The high activity of the prepared catalyst might be attributed to the cooperative activation of hydroxyl groups of BMP by both copper and cobalt in the catalyst, which facilitates the attack of phenols and condensation reaction of phenol with BMP.

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