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Mesoporous magnetic supported Cu complex for one-pot synthesis of 5-substituted 1*H*-tetrazoles in green media and the oxidation of sulfides

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We used the copper Phthalocyanine (Pc) on magnetic mesoporous silica nanoparticles. Therefore, several coordination sites became available which enhance chelating potency to load appropriate amounts of Gadolinium (Gd). This improves the catalytic activity in converting nitrile to tetrazole and selective oxidation of sulfides. Gadolinium (Gd) with incompletely occupied 4*f* and empty 5*d* orbitals can be used as the active component or as the promoter of the catalyst. Here, we outline the synthesis, characterization, and catalytic activity of a novel Gd(III) copper Phthalocyanine (Pc) coordination on the $CoFe_2O_4$/SBA-15 ($CoFe_2O_4$/SBA-15/CuPc@Gd). The prepared material was characterized using powder X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, elemental mapping, vibrating-sample magnetometer (VSM), Inductively coupled plasma atomic emission spectroscopy (ICP-AES), Fourier transform infrared spectroscopy, and nitrogen adsorption–desorption isotherm. The $CoFe_2O_4$/SBA-15/CuPc@Gd composite consists of a mesoporous structure with a surface area by BET and t-plot of 122.2 m^2/g and 86.28 m^2/g respectively, with a mean pore size of 5.37 nm, and pore volume of 0.164 cm^3/g. The $CoFe_2O_4$/SBA-15/CuPc@Gd was successfully applied as a powerful catalyst for green synthesis of 5-substituted 1*H*-tetrazoles in water and selective oxidation of sulfides at room temperature. This catalyst was recovered and reused several times without a significant decrease in efficiency and stability. The catalyst could be fully recovered by an external magnetic field and showed good reusability.

Phthalocyanines (Pcs) have been used in solar cells, sensors, semiconductors, photodynamic treatment (PDT), catalysis, coloring dyes for clothes and plastics, and several applications[1–4]. These macrocycles, comprised of four isoindole units connected by aza bridges, also feature a rich metalation chemistry that allows several metal ions in their core. These ions vary in size and charge, directly affecting the macrocycles' photochemical and photophysical properties allowing customization based on the application[5]. Under mild conditions, MPcs are considered effective catalysts for the oxidation of hydrocarbons, phenols, alcohols, and other organic molecules as well as the degradation of contaminants[6–8]. Pcs have superior performance over porphyrins in some cases, making them a great option for artificial biomimetic catalysts. Compared to porphyrin derivatives, the Pc-based catalysts have additional benefits that are generally associated with their structural, chemical, and thermal stability, cost-effectiveness, and capacity for large-scale manufacturing. However, Pcs' strong aggregation tendency and lack of solubility in common solvents make them unsuitable as catalysts in homogenous environments. Moreover, under typical catalytic circumstances, homogeneous catalysts based on Pcs tend to break down because of Pc auto-oxidation, which makes it difficult for these compounds to be recovered and reused[3]. Several methods to immobilize the core catalysts (Pcs) have already been researched and developed to solve these issues[7,9–11].

One of the important approaches of green chemistry is the use of recyclable catalysts[12,13]. Although homogeneous catalysts have many advantages such as high efficiency and selectivity, but from the point of

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view of green chemistry, there are drawbacks in the separation and recycling of catalysts from the product such as tedious and time-consuming work-up procedures. This problem is a big challenge especially when the expensive catalyst is used in large quantities[14–16]. A great deal of attention has been paid to develop methods for heterogenizing homogeneous catalysts to combine the advantages of both homogeneous and heterogeneous catalysis[17]. The immobilization of homogeneous catalysts on a large variety of organic or inorganic supports such as silica materials, zeolites, organosilica materials, aluminas, magnetic nanoparticles, polymers, biochar, and carbon materials to create heterogeneous catalysts is an effective strategy that has been developed in recent years[18–25].

Many distinct mesoporous materials with large volume, pore size, and surface area have already been synthesized using various surfactant templating strategies. These materials' unique functional applications in the field of heterogeneous organic catalysts are developed by utilizing the immobilization of organic functional groups[26–30]. Over the past ten years, many researches have been done on customized mesoporous materials with lots of active sites[31]. Among various supports, mesoporous silica materials, because of their various advantages such as high surface area, tunable pore size, nanometer sized pore, great chemical and mechanical stability, and controlled size have attracted much attention[14]. Customizing the surface area properties of mesoporous silica through organo-functional modification is advantageous for several applications within the realm of heterogeneous catalysis[32–34]. Li et al. used the three siliceous materials as VPO supports for both n-butane and propane partial oxidation. The $(VO)_2P_2O_7$ have been successfully supported onto SBA-15, MCM-41, and fumed SiO_2. As revealed by XPS and small-angle XRD results, the highest VPO dispersion was observed over the SBA-15 sample, while the lowest VPO dispersion was observed over the nonporous fumed SiO_2 sample[35]. The siliceous support SBA-15 has thermal stability, wide surface area, large pore volume, and uniform pore-size distributions, which makes it an appropriate choice for the binding of organo-catalysts[36–38]. Furthermore, SBA-15 is a promising porous solid due to its capacity to host a wide range of functional groups through co-condensation, isomorphic replacement, or grafting[39]. This presents a highly valuable opportunity to develop solids with very specific characteristics for use in pharmaceutical applications such as drug delivery, biosensing, and catalysis, as well as industrial applications related to adsorption processes and membrane separation[40–44]. To develop effective heterogeneous catalysts, magnetically responsive systems are an excellent alternative to catalyst systems. However, filtration or centrifugation are tedious and time-consuming methods of separating these particles from the reaction mixture. Magnetic nanoparticles (MNPs), which are easily separated from the reaction medium by applying an external magnetic field, could be used to solve this problem. In fact, the integration of magnetic nanoparticles with mesoporous silica nanoparticles generated a novel support that possesses the features and benefits of both mesoporous silica and magnetic nanoparticles[14].

Due to their environmental compatibility, stability, and ease of synthesis, spinel ferrites, MFe_2O_4 (M = Fe, Mn, Co, Ni, Cu, Zn), have recently attracted significant attention in the fields of magnetic resonance imaging, controlled drug release, superparamagnetic materials, electrocatalytic energy conversion, biosensing, and organic pollutant degradation[45–51]. Due in large part to their synergistic intermetallic contacts and magnetic recovery capabilities, they have been employed extensively as heterogeneous catalysts in numerous organic processes[52,53]. $CoFe_2O_4$ nanoparticles have a broad range of uses in drug delivery, magnetic storage, and magnetic response imaging due to their high saturation magnetization, specific surface areas, and coercivity[54–57].

Tetrazole is one of the heterocyclic compounds that consists of a five-membered ring and contains four nitrogen atoms and one carbon atom[58,59]. Tetrazoles have important features due to their many uses in various industrial and synthetic processes[60–62]. Among the drug compounds containing tetrazole ring, we can mention antibacterial drug, antimicrobial, antiviral, antidiabetic, antischizophrenic, antihypertensive drug, and cyclooxygenase-2 inhibitor[63–67]. Also, tetrazoles have applications as ligands in coordination chemistry and catalysis technology, as stable surrogates for carboxylic acids in medicinal chemistry, as effective stabilizers of metallopeptide structures in organometallic chemistry, etc.[15,68–71]. The synthesis of tetrazole ring is a vital step in organic and medicinal chemistry, and various methods have been provided for the synthesis of these compounds[16,25,67,70].

Sulfur compounds are one of the main sources of environmental pollution. Removing sulfur from petroleum compounds is a very important part of modern refining. Oxidation reactions are one of the simple and efficient methods for the transformation of organic functional groups[61,72]. This method selectively oxidizes sulfur-containing organic compounds to sulfoxide or sulfone. Sulfoxide derivatives are an important material in organic chemistry[73,74]. Also, sulfoxide derivatives have some biological activities such as antiulcer, antibacterial, antifungal, antiatherosclerotic, and anti-hypertensive[75–78].

Many homogeneous and heterogeneous catalysts were used to prepare tetrazoles, the results of some conversion of nitrile to tetrazole based on copper, boehmite, non-magnetic, magnetic, MCM-41, carbon, and ZnO nanoparticle catalysts are summarized in Table 1. Although many of these catalysts are efficient in the synthesis of tetrazole derivatives, many of them have one or more of the following difficulties: use of organic solvents, long times, high temperature, non-reusability of the homogeneous catalyst, low tetrazole yields, toxic reaction conditions, formation of side product such as stable metal-tetrazole complexes and tiresome workup of the reaction mixture. Therefore, it is highly desirable to progress an efficient catalyst for the selective synthesis of tetrazole under mild reaction conditions in a benign environmental solvent. The $CoFe_2O_4$/SBA-15/CuPc@Gd exhibits better reaction time, and recyclability under mild conditions.

Rare earth elements having incompletely occupied 4f and unoccupied 5d orbitals can be employed as an active component or a catalytic promoter[79,80]. Meng et al. recently showed that adding an appropriate amount of samarium (Sm) to MnO_x (Sm/Mn = 0.1) can improve the low-temperature performance of MnO_x as well as the stability against water vapor and sulfur toxicity[81]. Sun et al. discovered that adding europium (Eu) to MnOx improves SCR performance and resistance to water vapor and sulfur toxicity, as well as broadening the working temperature window[82], Similarly, Zhu et al. found that doping holmium (Ho) improved the catalytic activity

Entry	Catalyst	Catalyst loading (mg or mol%)	T (°C)	Solvent	Time (h)	Yield (%)	References
1	Boehmite@SiO$_2$@Tris-Cu(I)	0.2 mol%	120	PEG (Poly (ethylene glycol)-400	120	89	[91,92]
2	BNPs@Cur-Ni	40 mg	120	PEG-400	75 min	97	[91,93]
3	Cu-Guanidine@BO-NPs	40 mg	120	PEG-400	70 min	95	[91,94]
4	Pd-SMTU @boehmite	20 mg	120	PEG-400	2.5	95	[91,95]
5	Pd-Arg@boehmite	25 mg	120	PEG-400	7	97	[91,96]
6	Pd-isatin@boehmite	35 mg	120	PEG-400	7	96	[97]
7	CoFe$_2$O$_4$@glycine-Yb	70 mg	120	PEG-400	2.33	93	[98]
8	Methionine@Fe$_3$O$_4$	50 mg	120	DMSO	0.166	100	[99]
9	Fe$_3$O$_4$@SiO$_2$-APTES-TFA	100 mg	80	Ethanol	4	97	[100]
10	Cu-TBA@biochar	0.78 mol%	130	PEG	7	98	[101]
11	SBA-15@glycine-Cu	40 mg	100	PEG	110 min	98	[102]
12	Cu (II)-DCC-CMK-3	20 mg	120	PEG	90 min	97	[103]
13	Cu-MOFs-2 (Cu-TMU-17-NH$_2$)	50 mg	110	PEG	5	95	[104]
14	SO$_3$H@MCM-41	50 mg	80	DMF	1.6	90	[105]
15	Pd-SBT@MCM-41	35 mg	120	PEG-400	6.75	97	[106]
16	L-Cysteine@MCM-41	2.9 mol%	100	PEG-400	2.5	97	[107]
17	Ni-cytosine@MCM-41	0.1 mol%	120	PEG-400	1	92	[108]
18	Fe$_3$O$_4$@MCM-41-SB-Cu	30 mg	120	DMF	1	95	[14]
Entry	Carbon-based nano-catalyst	Catalyst loading (mg or mol%)	T (°C)	Solvent	Time (h)	Yield (%)	References
19	ZrFe$_2$O$_4$@SiO$_2$–N–(TMSP)–ASP–Pd$^{(0}$	15 mg	120	PEG-400	8	97	[109]
20	[Fe$_3$O$_4$@TAM-Schiff-base Cu (II)]	25 mg	120	PEG-400	100	98	[110]
21	Fe$_3$O$_4$-CNT-TEA-Cu (II)	5 mg	70	DMF	1.50	96	[111]
22	GO/Fe$_3$O$_4$@PAA-Cu-complex	20 mg	100	PEG-400	7	98	[112]
23	ZnO	100 mg	120–130	DMF	14	69–82	[113]
24	ZnO/Co$_3$O$_4$	50 mg	120	DMF	12	90	[114]
25	MnCl$_2$.4H$_2$O	10 mol %	120	DMSO	1	92	[115]
26	Pd/AlO(OH) NP	30 mg	78	EtOH	4	73	[116]
27	Fe$_3$O$_4$@MCM-41@Cu-P2C	20 mg	120	PEG	3.5	95	[117]
28	CoFe$_2$O$_4$/SBA-15/CuPc@Gd	100 mg	Boiling point	H$_2$O	60 min	65	This Work

Table 1. Catalytic performance of different catalysts for the synthesis of 5-substituted-1H-tetrazole via a [3 + 2] cycloaddition reaction.

of the Fe–Mn/TiO$_2$ catalyst[83]. These successful studies confirm that rare earth elements can be used to boost the catalyst. Gadolinium (Gd) is a lanthanide situated in the middle of the periodic table that has been used in different fields, mainly for magnetic resonance imaging contrast agents, due to the unusual magnetic properties of the Gd(III) ion[84]. In detail, the Gd(III) has seven unpaired electrons on each orbit which can give rise to large magnetic moments[84]. In addition, Gd as dopant can also be conductive in improving the photocatalytic performances of TiO$_2$, MoO$_3$, and Bi$_2$MoO$_6$[85–88], the dry reforming of methane for Ni/ZSM-5 catalysts[89], and the ethanol oxidation and ethylene production of Cr$_2$O$_3$[90].

One of the important approaches in green chemistry is the tendency to development of recyclable catalysts. Another principle of green chemistry is the use of green solvents and the replacement of highly toxic and volatile organic solvent. We used copper Phthalocyanine (Pc) on magnetic mesoporous silica nanoparticles. Therefore, several good coordination sites are available that enhance chelating potency to load appropriate amounts of Gadolinium (Gd) and therefore improve catalytic activity in converting nitrile to tetrazole and selective oxidation of sulfides. Gadolinium has rarely been reported as a catalyst for the synthesis of organic compounds. This is the first time for reactions of CoFe$_2$O$_4$/SBA-15 supported copper Phthalocyanine (Pc), with Gd salts. For effective synthesis of tetrazole and selective oxidation of sulfides. The reactions are based on green chemistry under mild reaction conditions in green solvent. At a relatively low temperature compared to the reported work, tetrazole derivatives are prepared in water solvent with good efficiency.

Material and methods
Preparation of the CoFe$_2$O$_4$ nanoparticles
To produce CoFe$_2$O$_4$ nanoparticles using the coprecipitation method, 50 mL of distilled water was used to dissolve 0.5 mmol of CoCl$_2$·2H$_2$O powder and 1 mmol of FeCl$_3$·6H$_2$O powder. while being gassed with nitrogen. The first solution was then gradually supplemented with 25 mL dissolved NaOH (1 g. 25 mmol). For three hours, the final solution was refluxed. Following the reaction's cooling to room temperature, the black precipitate that

had formed was separated using a magnet. The resulting $CoFe_2O_4$ nanoparticles were subsequently washed with ethanol and dried at 61 °C[118].

Preparation of the SBA-15

First, 30 mL of H_2O and 90 mL of HCl (2 M) were combined with 4.0 g (0.7 mmol) of Pluronic P123, then the mixture was agitated at 30 °C for 5 h. Subsequently, after gradually adding tetraethylorthosilicate (9.04 mL, 40 mmol), the mixture was agitated for 20 h. After being separated, the outcome was washed, dried, and stored. The sample then received a 5-h calcination at 823 K[119].

Preparation of the CoFe₂O₄/SBA-15

Using the wet impregnation approach, 2.0 g (8.5 mmol) of $CoFe_2O_4$ nanoparticles were added to a mixture of ethanol and deionized water (1:1). Following a 20-min sonication process to disperse the solution, 1.72 g (28.7 mmol) of SBA-15 and 5 mL of aqueous ammonia were added. The mixture was stirred for a further 24 h at room temperature. Following their separation using an external magnet, they were rinsed using deionized water and ethanol, the resulting $CoFe_2O_4$/SBA-15 nanocomposite was dried for 12 h at 80 °C.

Preparation of the CoFe₂O₄/SBA-15/CuPc@Gd

30 mL of DMF was used to dispersion of 30 mg of $CoFe_2O_4$ /SBA-15, and subjected to a 1-h sonication. Subsequently, a solution of 10 mg (17.3 mmol) of copper(II) phthalocyanine in dimethyl formamide (DMF) was added. One more thirty minutes were spent sonicating the solution and then it was stirred continuously for another 24 h. Following that, finally, the dark samples were centrifuged, and the solid was washed three times with DMF and twice with ethanol before being dried for 12 h at 80 °C. After that, 1 g $CoFe_2O_4$/SBA-15/CuPc with 30 mL of ethanol solvent and 2 mmol of Gd $(NO_3)_3$ were combined, and the reaction mixture was refluxed for 24 h (Fig. 1).

Spectral data

5-(3-Nitrophenyl)-1*H*-tetrazole
(Table 4, Entry1): ^{1}HNMR (400 MHz, DMSO, ppm): δ 8.88 (s, 1H), 8.48–8.51 (m, 2H), 7.90–7.97 (m, 1H).
5-(4-Nitrophenyl)-1*H*-tetrazole
(Table 4, Entry 2): ^{1}HNMR (400 MHz, DMSO, ppm): δ 8.50–8.53 (d, 2H), 8.40–8.44 (d, 2H).
5-(4-Bromophenyl))-1*H*-tetrazole
(Table 4, Entry 4): ^{1}HNMR (400 MHz, DMSO, ppm): δ 7.87–7.89 (m, 4H).
Methyl phenyl sulfoxide
(Table 6, Entry 1): ^{1}HNMR (400 MHz, CDCl₃, ppm): δ 2.98 (s, 3H), 7.46– 7.48 (m, 2H), 7.55–7.59 (m, 1H), 7.85–7.87 (m, 2H).
Dibenzyl Sulfoxide
(Table 6, Entry 5): ^{1}HNMR (400 MHz, CDCl₃, ppm): δ 4.16 (s, 4H), 7.40–7. 45 (m, 10H). Benzyl phenyl sulfoxide
(Table 6, Entry 7): ^{1}HNMR (400 MHz, DMSO, ppm): δ 4.68 (s, 2H), 7.14–7.16 (m, 2H), 7.28–7.34 (m, 3H) 7.53–7.62 (m, 2H) 7.71–7.75 (m, 3H).
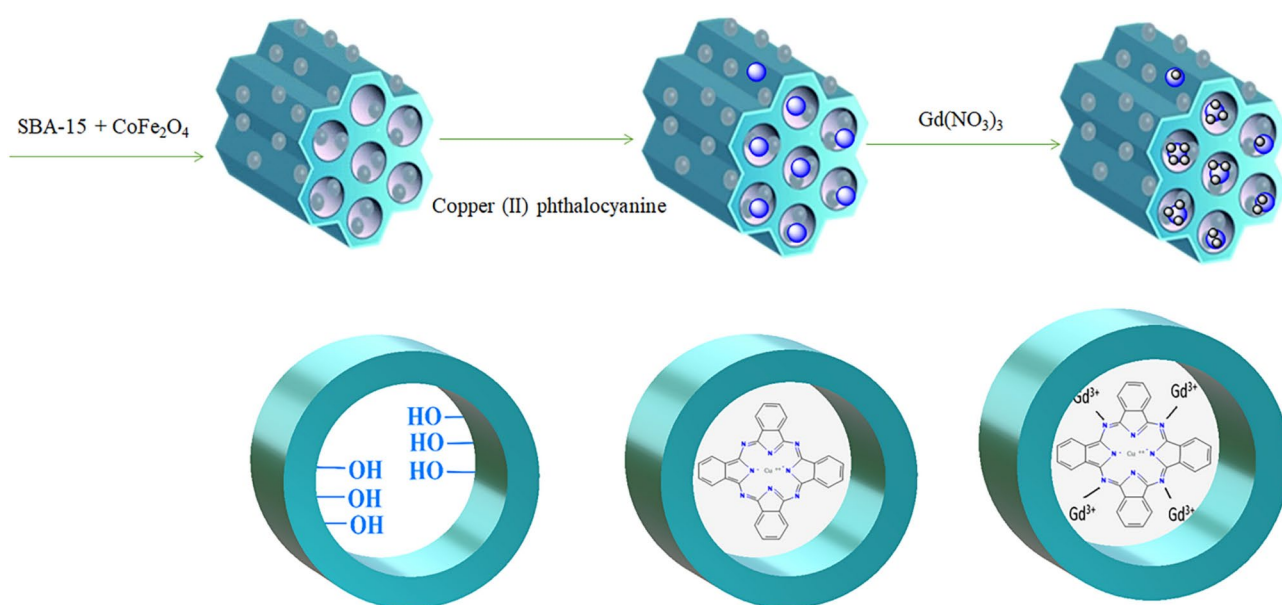

Fig. 1. Diagrammatic representation of the synthesis of the $CoFe_2O_4$/SBA-15/CuPc@Gd.

Results and discussion
Catalyst characterization
XRD analysis

The XRD patterns for the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd catalysts are shown in Fig. 2. All samples' XRD profiles display the distinctive diffraction peaks at rounds 18.3, 30.2, 35.6, 43.0, 53.5, 57.1, and 62.7°, which are attributed to the spinel ferrite type $CoFe_2O_4$ (JCPDS No. 22-1086) (111), (220), (311), (400), (422), (511), and (440) planes[120]. No impurity peaks were detected in any of the samples. The XRD of $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd reveal that the $CoFe_2O_4$ support remains structurally unchanged, this demonstrates the $CoFe_2O_4$'s phase preservation during the functionalization processes. $CoFe_2O_4$ magnetic nanoparticles retain their crystalline structure because the coated silica becomes amorphous. The diffraction peak at $2\theta = 71.0°$ in the XRD of the $CoFe_2O_4$/SBA-15/CuPc@Gd may result from species of metallic copper[121]. This peak was not observed in the XRD patterns for the $CoFe_2O_4$/SBA-15. The small angle XRD pattern of the mesoporous SBA-15 displays one strong peak indexed as (100) planes and two weak peaks corresponding to (110) and (200) planes of the 2D hexagonal mesoporous structure[122]. The low-angle XRD patterns of the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd were also investigated as depicted in Fig. 3. The XRD pattern of the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd gives only one peak at low angle corresponding to (100) plane, which indicated that the mesostructure was retained[123]. The two peaks corresponding to the (110) and (200) planes do not exist in the XRD patterns $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd. This result could be attributed to the lowering of local order[14].

FE-SEM, mapping, and HRTEM analysis

According to the HRTEM image, the $CoFe_2O_4$/SBA-15/CuPc@Gd showed a roughly spherical morphology with a gray SBA-15 and black CoFe2O4, suggesting that the $CoFe_2O_4$ is evenly distributed throughout the SBA-15 silica. HRTEM images of the $CoFe_2O_4$/SBA-15/CuPc show a pore wall region (Fig. 4). To illustrate the shape of the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd, FE-SEM images were acquired (Fig. 5). The FE-SEM images of the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd verify that SBA-15 particles and $CoFe_2O_4$ nanoparticles are present in the $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd composites. Figure 4 shows that the $CoFe_2O_4$ and CuPcS particles, which have an average size of roughly 15–30 nm, are fairly evenly distributed onto SBA-15.

To map the presence of elementals analysis, the EDS spectra and elemental mapping were used. The elemental mapping of the $CoFe_2O_4$/SBA-15/CuPc@Gd catalysts is given in Fig. 6. The desired elements are shown for $CoFe_2O_4$/SBA-15/CuPc@Gd. The EDS spectra for $CoFe_2O_4$/SBA-15/CuPc@Gd also shows the desired elements.
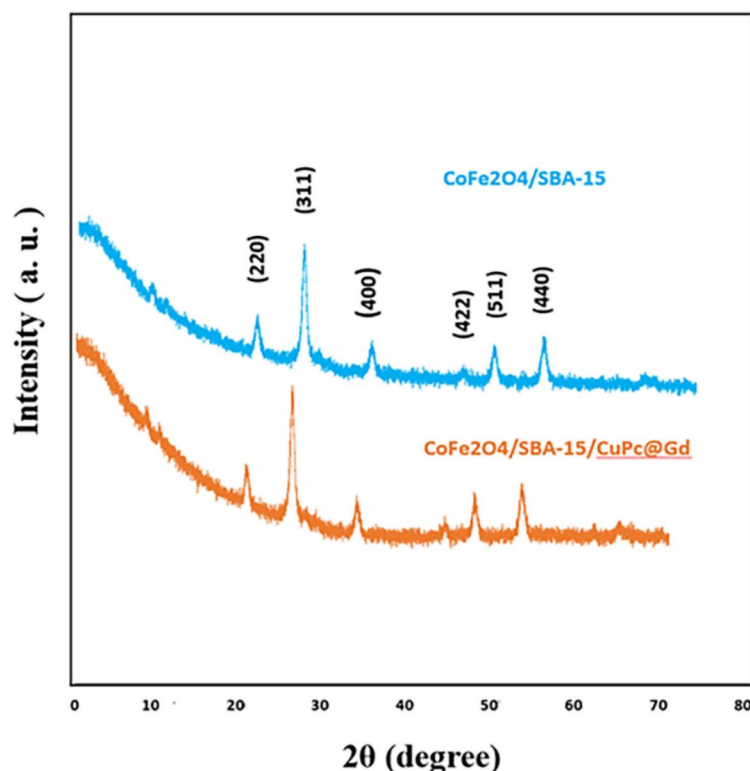
Fig. 2. Wide angle X-ray diffraction patterns of the $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd.
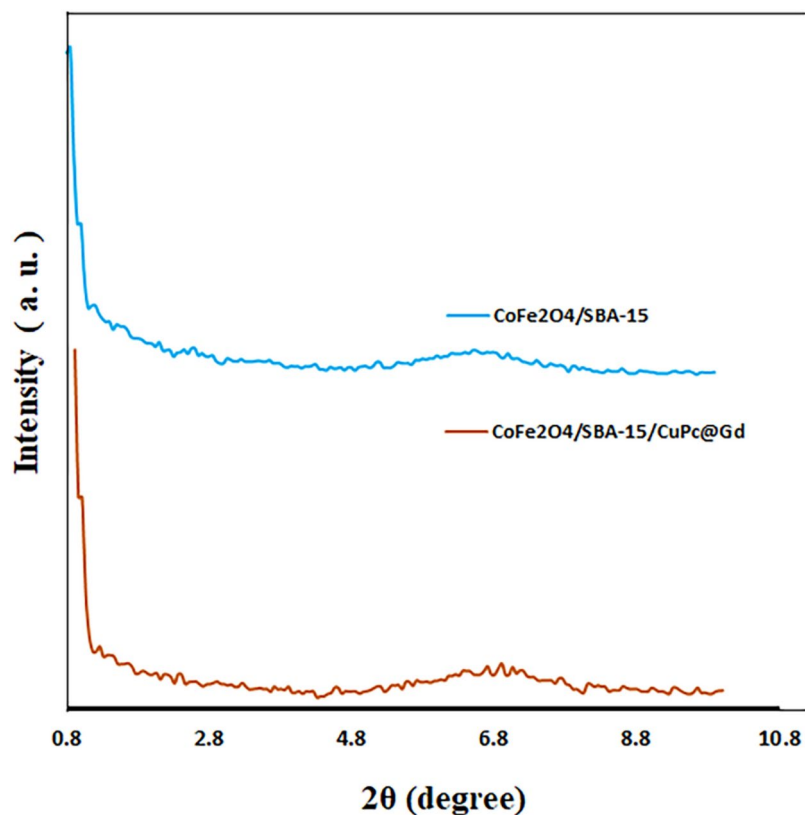
Fig. 3. Low angle X-ray diffraction patterns of the $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd.

Magnetic properties
Magnetization loops of $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd at the room-temperature are shown in Fig. 7. The samples' magnetization would almost reach saturation at 10,000 Oe of the applied magnetic field. $CoFe_2O_4$/SBA-15 had saturation magnetization (Ms) of 8.32 emu/g and remnant magnetization (Mr) of 2.25 emu/g, respectively, indicating a normal ferromagnetic hysteresis. As shown in the figure, the remnant magnetization (Mr), and saturation magnetization (Ms) values of $CoFe_2O_4$/SBA-15/CuPc@Gd magnetite particles are equal to 1.66 emu/g, and 6.08 emu/g respectively, which is lower than uncoated magnetite nanoparticles. This decrease in magnetism is due to the presence of a complex around $CoFe_2O_4$ nanoparticles.

N_2 adsorption–desorption isotherms
The BET and t-plot were used to measure the surface area, and the BJH method were used to examine the textural properties of $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd. The H1 hysteresis loop for a type IV adsorption–desorption isotherm which is seen in Fig. 8 demonstrates the presence of channels with a mesopore aspect in $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd[124]. The surface area (Brunauer–Emmett–Teller (S_{BET}) method), surface area (t-plot method (S t-Plot)), average pore sizes (d_{avg}) and total pore volumes (V_{total}) of $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd are shown in Table 2. Based on the given information, it can be observed that the BET and t-plot method show surface area of 158.89 m^2/g and 133.11 m^2/g respectively for $CoFe_2O_4$/SBA-15, also mean pore size is 7.00 nm, and pore volume is 0.276 cm^3/g. The $CoFe_2O_4$/SBA-15/CuPc@Gd shows a surface area by BET and t-plot of 122.2 m^2/g and 86.28 m^2/g respectively, with a mean pore size of 5.37 nm, and pore volume of 0.164 cm^3/g. The decrease in surface area signifies the binding of organic species on the mesopore surface and the decrease in the volume of the pores proves that the desired species is positioned inside the pores. Additionally, the distribution of BJH pore sizes was between 1 and 8 nm for the $CoFe_2O_4$/SBA-15 and 1–5 nm for the $CoFe_2O_4$/SBA-15/CuPc@Gd (Fig. 9).

FT-IR analysis
The infrared spectra of the synthesized samples were investigated and they can be seen in Fig. 10.

The signals at approximately 587 cm^{-1} in all curves correspond to the Fe–O bond's stretching modes. In the infrared spectrum of SBA-15, an absorption band is observed in the region of 1000–1300 cm^{-1} due to Si–O–Si asymmetric stretching vibrations.

The signals detected at about 463 cm^{-1} can be associated with the rocking motion of the bridging oxygens band in Si–O–Si, and the symmetric stretching vibration of Si–O–Si bonds can be coupled with the 803 cm^{-1}. The band at around 3200–3700 cm^{-1} is related to the surface hydroxyl groups stretching vibrations of the silanol group (Si–OH). The band at the 1623–1650 cm^{-1} region is due to the H–O–H bending vibration. In the infrared
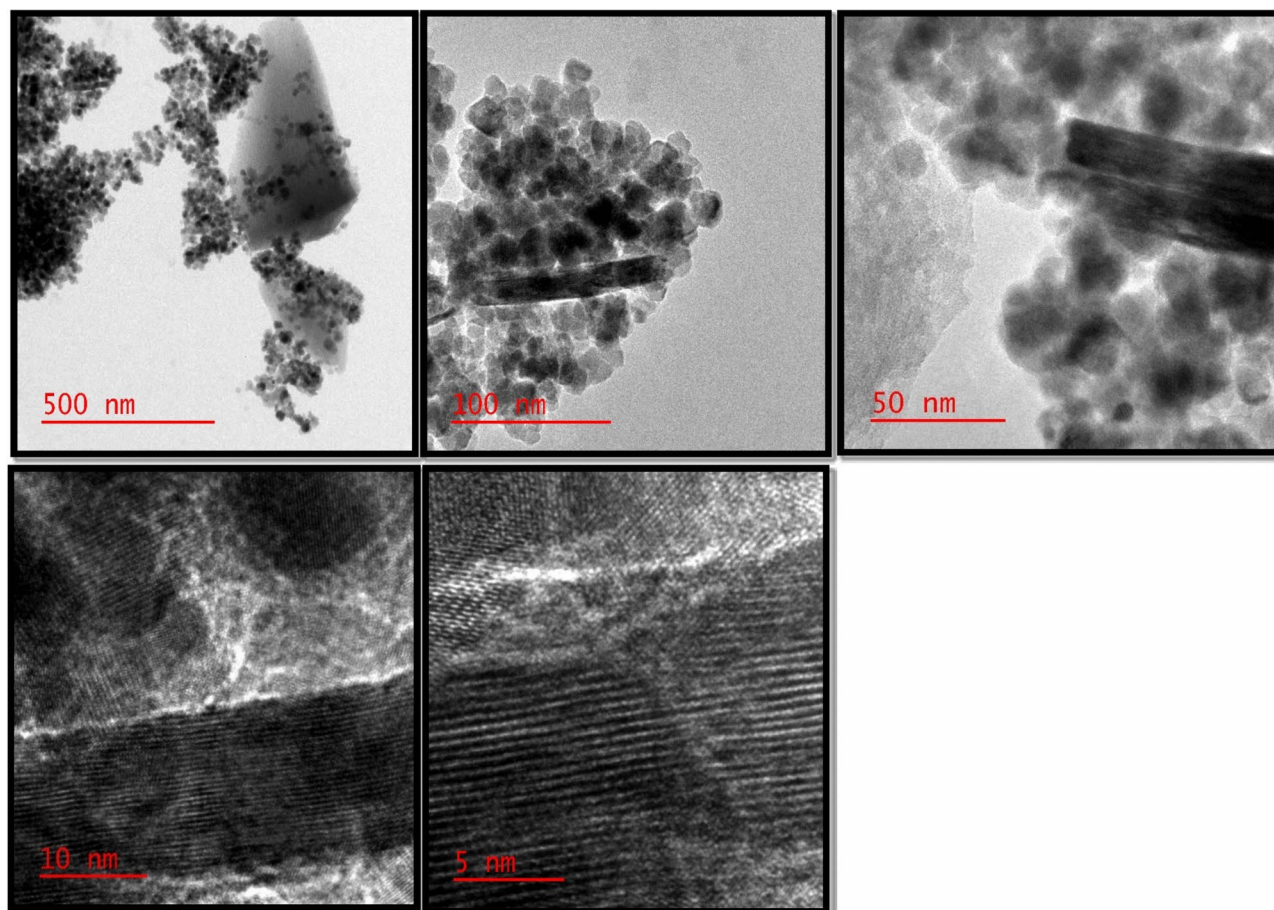
Fig. 4. HRTEM and EDX of $CoFe_2O_4$/SBA-15/CuPc@Gd.

spectrum of $CoFe_2O_4$/SBA-15 the extra band at 960–970 cm^{-1} appears, which is mostly attributed to the Si–OH vibration mode; however, when metals are added, the band becomes more intense and shifts to a lower wavenumber. It shows that SBA-15 silica has been added to the magnetite nanoparticles. In the reported article the FT-IR of CuPc, out-of-plane bending vibration of C–H bonds of the phenyl and porphyrin were related to bands at 735 and 845 cm^{-1}, respectively. Bands at 1113 and 1335 cm^{-1} were attributed to the C–H vibration of the porphyrin and phenyl, respectively. The 1437 and 1510 cm^{-1} bands can be corresponded to the C=C stretching vibration in porphyrin and phenyl ring, respectively. The 1628 cm^{-1} band may be attributed to the C=N stretching vibration in the porphyrin. Bands at 1635 cm^{-1} and 3430 cm^{-1} can be related to the bending and stretching vibrations of OH groups on the catalyst surface and water adsorbed on the surface[125]. After loading the CuPc, the new bands are observed in the FT-IR of the $CoFe_2O_4$/SBA-15. The new band around at 1422 cm^{-1} is related to the anchored complex copper phthalocyanine[126]. In the FT-IR spectrum of $CoFe_2O_4$/SBA-15/CuPc@Gd, the density of band at 1400 cm^{-1} attributed to C=C stretching vibration in porphyrin has increased.

Catalyst evaluation

The catalyst containing $CoFe_2O_4$/SBA-15 coated with Gd(III) copper phthalocyanine complex was used to prepare 5-substituted-1H-tetrazoles derivatives. The reaction of benzonitrile (1 mmol), catalyst, and NaN_3 (1.2 mmol) was chosen as a reaction sample. To optimize the reaction conditions, the efficiency of catalyst amounts, various solvents, and different temperatures have been studied.

Effect of solvent

Different solvents such as PEG (Poly (ethylene glycol), n-hexane, acetonitrile, EtOH, EtOH/water, and water in 1440 min were tested. The reaction yield in PEG was 68% (Table 3, entry 1). In acetonitrile solvent, the reaction yield was 40% (Table 3, entry 2). In hexane solvent, the reaction yield was 30% (Table 3, entry 3). In the EtOH solvent, the reaction yield was 60% (Table 3, entry 4). The reaction yield in EtOH/water (1:1) solvent is 62% (Table 3, entry 5). The reaction yield in the EtOH/water (2:1) solvent is 55% (Table 3, entry 6). The reaction in water solvent within 60 min, the yield was 65% (Table 3, entry 7). Accordingly, H_2O solvent was selected as the intended solvent for this method. The solvent dielectric constant has a major impact on the chemical intermediate's stabilization. Higher solvent dielectric constant reaction intermediates are stabilized by stronger ionic forces[127,128]. Water exhibited the greatest dielectric constant (80) of all the solvents, followed by acetonitrile
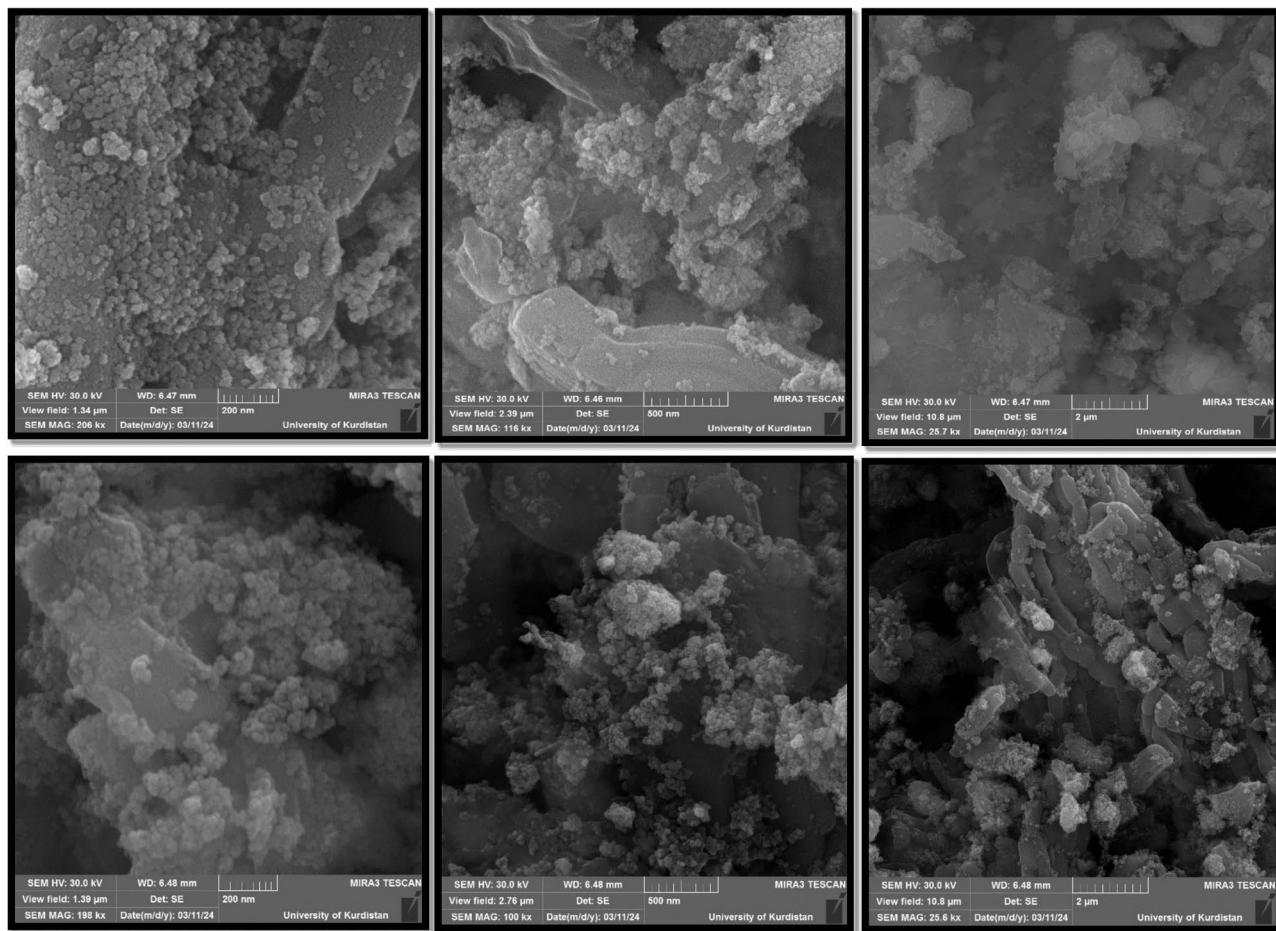
Fig. 5. SEM images of (up) $CoFe_2O_4$/SBA-15, and (down) $CoFe_2O_4$/SBA-15/CuPc@Gd.

(36.6), EtOH (24.3), and hexane (2.0), The degree of the reactants' solubility can be used to characterize the solvent impact. Derivatives of sodium azide dissolve more readily in water.

Effect of temperature
Different temperatures of Boling point, 60, and 40 ℃, were tested, based on Table 3 in H_2O solvent at boiling point, for 60 min the reaction yielded 65%. (Table 3, entry 7), and at a temperature of 60 °C in 80 min, the reaction yielded 57% (Table 3, entry 8), and at 40 °C in 120 min, the reaction yielded 55% (Table 3, entry 9). The temperature of the Boling point was chosen to continue the reaction process. The Arrhenius equation predicted that the reaction rate would rise with temperature[129]. The boiling point produced the best outcome for this reaction.

Effect of amounts of catalyst
The amount of catalyst was changed according to Table 3, and the value of 100 mg of catalyst was chosen (Table 3, entry 7). The abundance of active sites present in the sample framework is the cause of the maximal yield.

Using the optimized conditions, several tetrazole derivatives have been prepared with $CoFe_2O_4$/SBA-15/CuPc@Gd, which can be seen in Table 4. In this research, it has been tried to use different combinations of aromatic nitriles with electron withdrawing and electron donating groups. The ability to achieve successful conversion in a short time is a significant advantage of this method.

The formation of 1*H*-tetrazoles depends critically on the nitrile substrate's coordination with the Lewis acidic Gd (III). The Lewis acidic Gd (III) acts as an active site for the coordination of the nitrile molecule. The primary element affecting [2 + 3] cycloaddition is the coordination of Gd (III) to the nitrile. Tetrazole is the final result of further hydrolysis and azide nucleophilic assault. When the nitrile substrate coordinates with Gd^{3+}, it forms a stable complex that activates the nitrile toward nucleophilic attack. This coordination increases the electrophilicity of the carbon atom in the nitrile, making it more susceptible to nucleophilic attack by azide ions[130] (Scheme 1).

The oxidation of sulfides to sulfoxide for the catalytic activity of the catalysts was examined in the second section. A study was done on the best solvent to use, as well as the appropriate amount of catalyst and oxidant, to achieve the best conditions for carrying out the oxidation process of sulfides. For that, methyl phenyl sulfide oxidation was employed as a sample reaction at room temperature with various solvents in the presence of
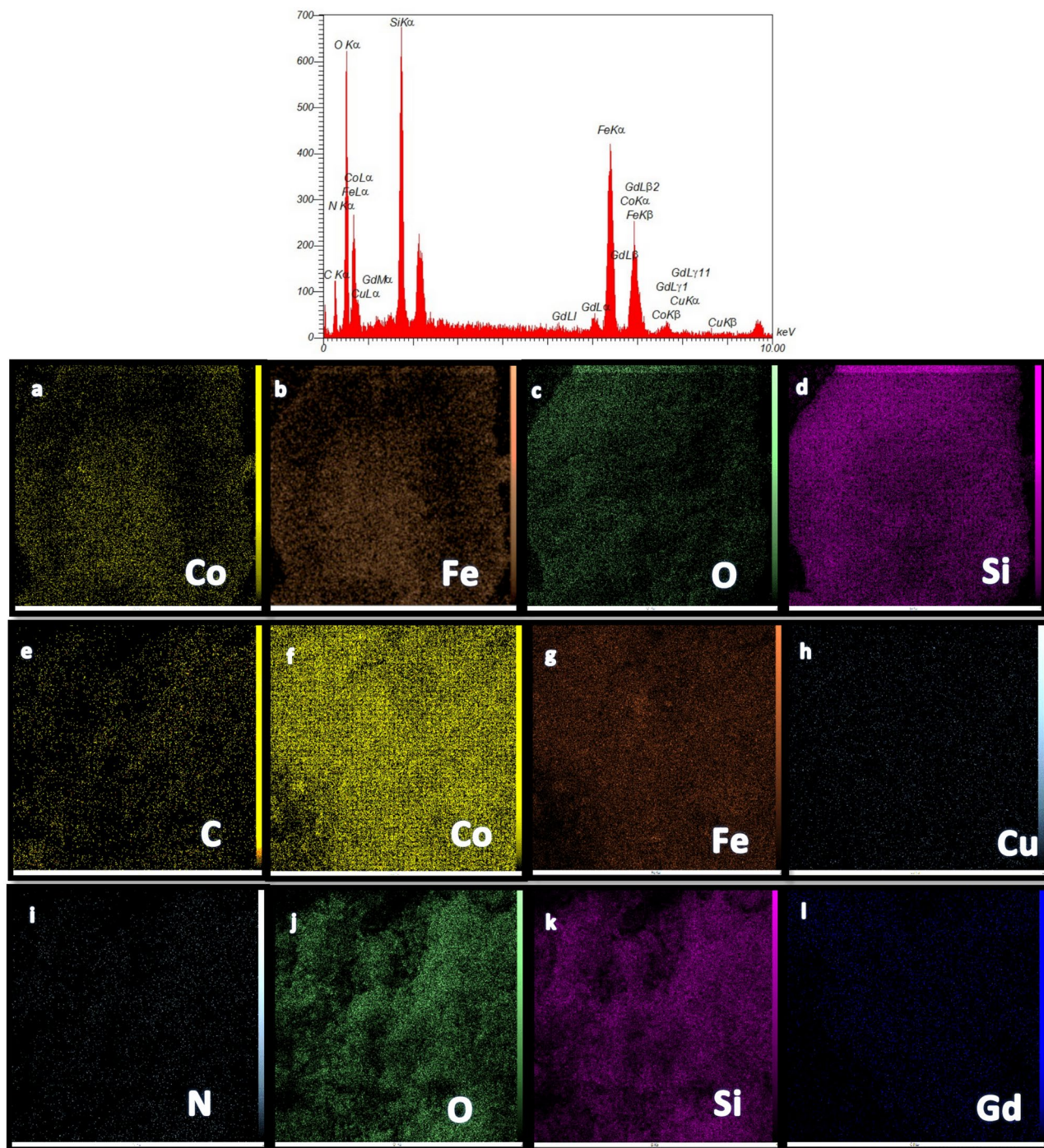
Fig. 6. EDX and Elemental mapping of (a-d) CoFe$_2$O$_4$/SBA-15, and (e-l) CoFe$_2$O$_4$/SBA-15/CuPc@Gd.

CoFe$_2$O$_4$/SBA-15/CuPc@Gd. Table 5 presents the survey's results. Initially, the reaction was screened using a variety of solvents, including acetonitrile, EtOH, and water. In this investigation, the maximum yield is seen in H$_2$O. The yields of the other solvents were lower.

The impact of catalyst weights (0, 4, 6, 8, and 10 mg) has also been investigated. The findings showed that the yield increased from 0% (0 mg) and 78% (4 mg) to 80% (6 mg) and finally to 91% (8 mg). The findings show that the catalyst's greatest yield was obtained at 8 mg, and that the product yields a little increased after 8 mg.

Additionally, we ran the process with varying concentrations of oxidant. The findings showed that the yield increased from 50% (0.1 mL), 80% (0.3 mL), and finally 91% (0.5 mL).

The most suitable amount required to complete this reaction was 8 mg of catalyst and 0.5 mL of H$_2$O$_2$, which produced the best results.
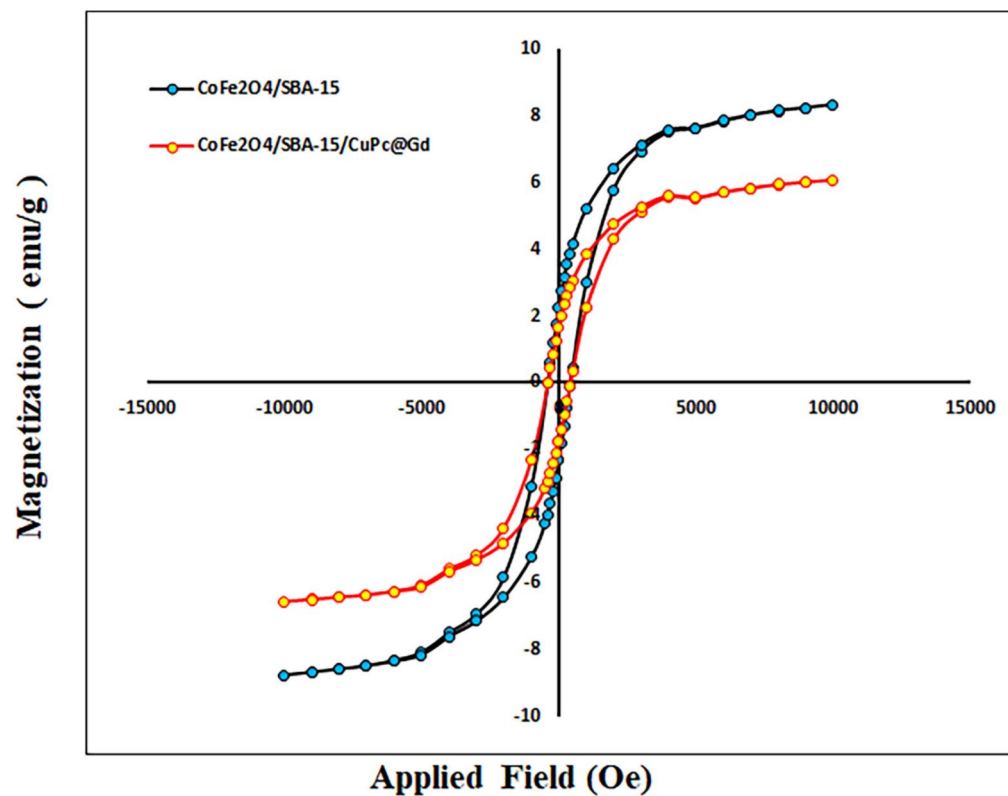
Fig. 7. Magnetization curves of CoFe$_2$O$_4$/SBA-15, and CoFe$_2$O$_4$/SBA-15/CuPc@Gd.
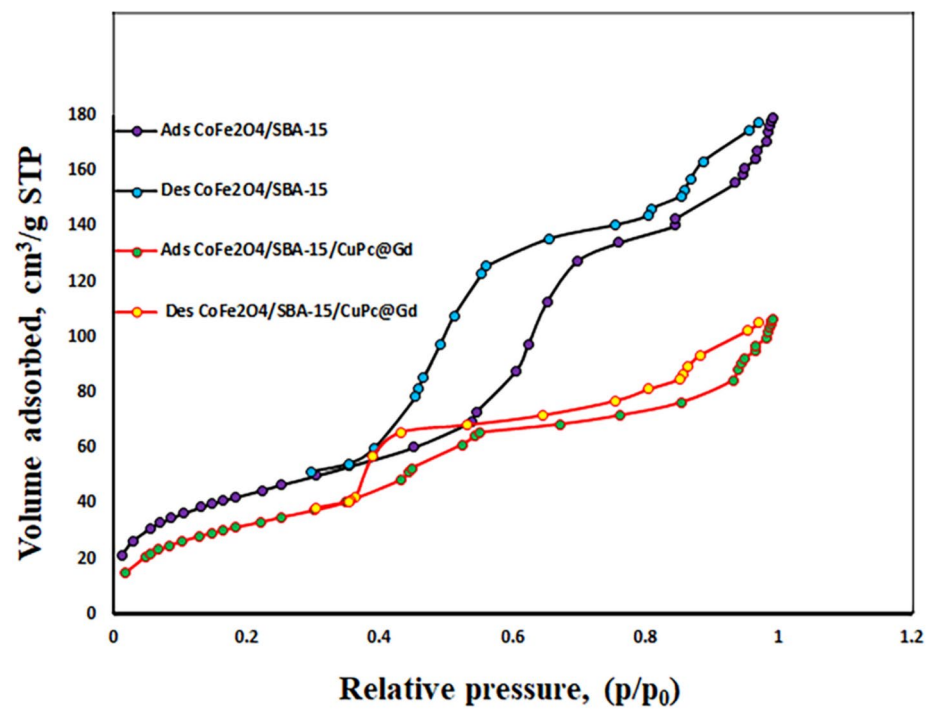
Fig. 8. N$_2$ adsorption–desorption isotherms of CoFe$_2$O$_4$/SBA-15, and CoFe$_2$O$_4$/SBA-15/CuPc@Gd.

Entry	Catalyst[b]	S_{BET} (m²/g)	$S_{t\text{-}Plot}$ (m²/g)	d_{avg} (nm)	V_{total} (cm³/g)
1	$CoFe_2O_4$/SBA-15	158.89	133.11	6.95	0.276
2	$CoFe_2O_4$/SBA-15/CuPc@Gd	122.2	86.28	5.37	0.164

Table 2. The study's synthesized samples' textural characteristics[a].
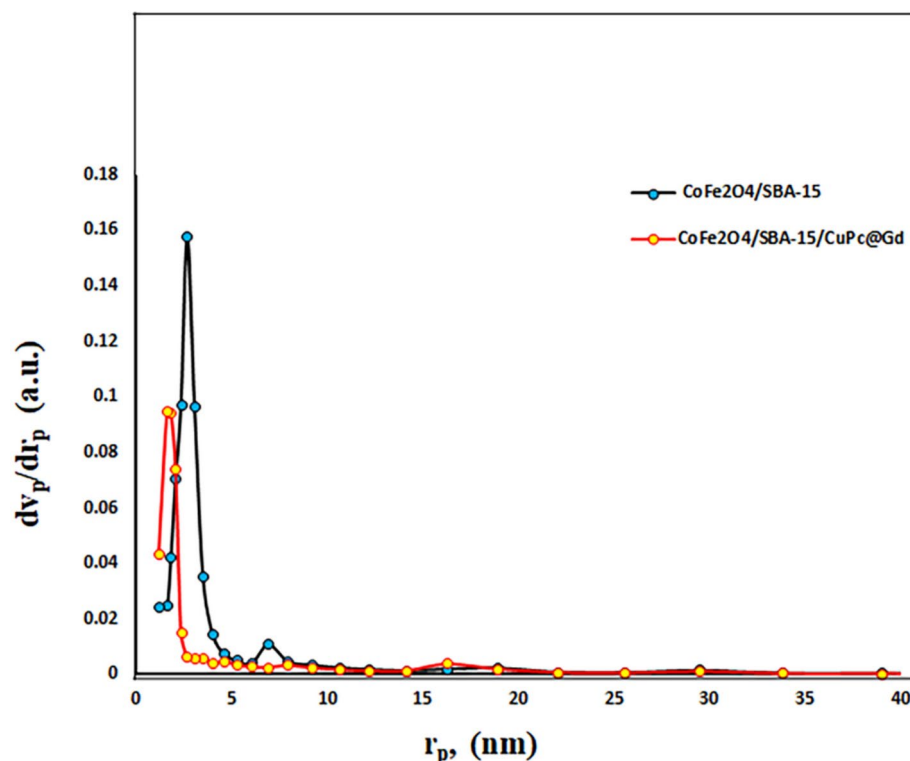
Fig. 9. BJH pore distribution of $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd.

After the ideal conditions had been achieved, as indicated in Table 6, a variety of sulfides with various functional groups were employed to produce sulfoxides, which resulted in the production of the intended products with a high yield and a short reaction time. This catalyst has been used to create both aliphatic and aromatic sulfoxides, as can be observed. These findings unequivocally demonstrate that this approach can be used to quickly and environmentally-friendly convert a wide range of derivatives, which is an enormous advantage in the field of green chemistry.

Based on the reported mechanism for the oxidation of sulfides into sulfoxides using hydrogen peroxide in the presence of a catalyst, one explanation for this process is the complex formation between the hydrogen peroxide and the M(III) (intermediate A). After the formation of [M^{III}-OOH], it may form oxo metal species as the active oxidant (intermediate B). This active species can oxidize organic sulfides by the formation of the oxidant-substrate complex (intermediate C) and the oxygen transfer to the organic substrate (Scheme 2 and 3)[133–136].

Homoselectivity and chemoselectivity

When there are two or more identical functional groups in a molecule, only one of them reacts selectively in the course of the reaction; this selectivity can be named homoselectivity[141,142]. $CoFe_2O_4$/SBA-15/CuPc@Gd catalyst shows a good homoselectivity in dicyano-functional benzonitriles, e.g., phthalonitrile (Table 4, entry 11) and terephthalonitrile (Table 4, entry 12) for the synthesis of corresponding tetrazoles (Scheme 4).

Chemoselectivity is the preferential reaction of one functional group in the presence of others[143,144]. Also, there is chemoselectivity in the oxidation of 2-(phenylthio) ethanol (Table 6, entry 6). In this substrate, the functional group of sulfide was converted to the sulfoxide, but alcohol oxidation did not occur during the conversion, and the primary hydroxyl group retained intact in the course of the reaction in the presence of H_2O_2 as oxidant (Scheme 5).

Catalyst reusability

The catalyst's capacity for recovery is one of the key responsibilities of green chemistry. After a reaction was completed, the catalyst was separated using a magnet and repeatedly rinsed with acetonitrile and ethanol for
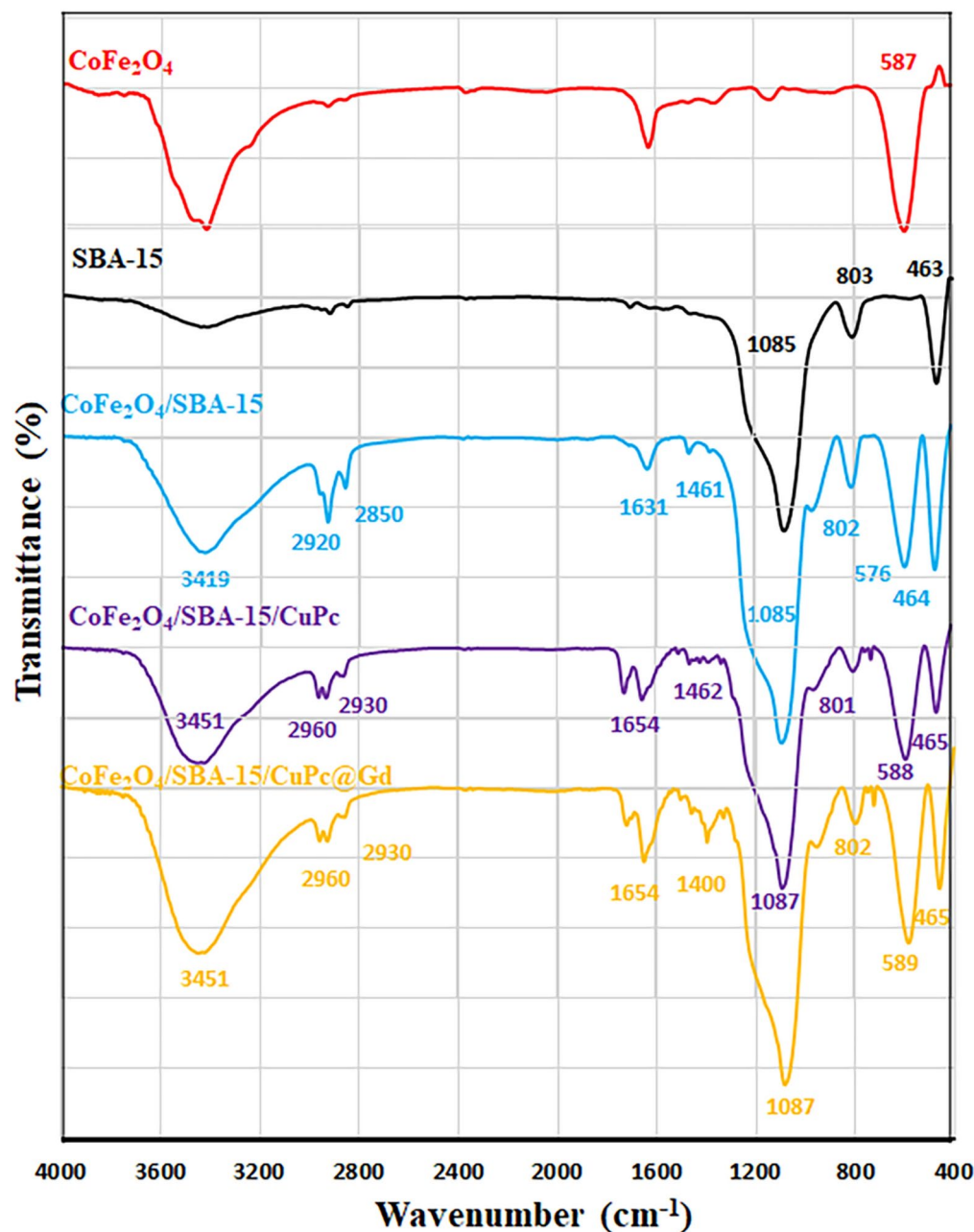
Fig. 10. FT-IR spectra of $CoFe_2O_4$, SBA-15, $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd.

catalyst recovery. Following an oven-drying process, it was reused in a fresh run with optimal parameters with benzonitrile (1 mmol), catalyst (100 mg), and NaN_3 (1.2 mmol), in an aqueous medium. The results for the heterogeneous catalyst that was used for the synthesis of tetrazole are shown in Fig. 11. As can be seen, without experiencing a significant reduction in its catalytic activity, the recovered catalyst was utilized five times in the process.

Leaching study

The leaching of the catalyst was investigated with ICP-AES (Inductively coupled plasma atomic emission spectroscopy). ICP-AES analysis of the fresh and recovered catalyst was investigated. Using the ICP-AES technique, the Gadolinium (Gd) quantity of the catalyst before and after the reaction for the preparation of 5-(4-chlorophenyl)-1*H*-tetrazole was determined. It was obtained that the quantity of Gadolinium (Gd) in the fresh $CoFe_2O_4$/SBA-15/CuPc@Gd catalyst is 0.7 mmol g^{-1}. Gadolinium (Gd) content has slightly decreased to 0.6 mmol g^{-1} after the 5th catalytic reaction cycle.

Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)ᵃ
1	PEG	100	120	1440	68
2	Acetonitrile	100	82	1440	40
3	Hexane	100	68	1440	30
4	EtOH	100	75	1440	60
5	H_2O /EtOH (1:1)	100	75	1440	62
6	H_2O /EtOH (1:2)	100	75	1440	55
7	H_2O	100	Boiling point	60	65
8	H_2O	100	60	80	57
9	H_2O	100	40	120	55
10	H_2O	80	Boiling point	70	62
11	H_2O	60	Boiling point	90	59
12	H_2O	40	Boiling point	140	60
13	H_2O	–	Boiling point	1440	Trace

Table 3. 1*H*-tetrazole yield at different solvents, catalyst amounts, and temperatures in the presence of $CoFe_2O_4$/SBA-15/CuPc@Gd Reactions conditions: Nitrile (1 mmol), solvent (3 mL), catalyst, and NaN_3 (1.2 mmol). ᵃIsolated yield.

Conclusion

We have prepared $CoFe_2O_4$/SBA-15/CuPc@Gd the mesoporous catalysts for converting nitrile to tetrazole in a single pot and oxidation of sulfides. It is confirmed by the X-ray diffraction patterns of the spinel ferrite type for $CoFe_2O_4$/SBA-15/CuPc@Gd. The FE-SEM images of the $CoFe_2O_4$/SBA-15 and $CoFe_2O_4$/SBA-15/CuPc@Gd verify that SBA-15 particles and $CoFe_2O_4$ nanoparticles are present in the $CoFe_2O_4$/SBA-15, and $CoFe_2O_4$/SBA-15/CuPc@Gd composites. The $CoFe_2O_4$, CuPc, and Gd (III) particles, which have an average size of roughly 15–30 nm, are fairly evenly distributed onto SBA-15. The EDS spectra and elemental mapping show the desired elements for $CoFe_2O_4$/SBA-15/CuPc@Gd. The remnant magnetization (Mr) and saturation magnetization (Ms) values of $CoFe_2O_4$/SBA-15/CuPc@Gd magnetite particles are equal to 1.66 emu/g, and 6.08 emu/g respectively, which is lower than uncoated magnetite nanoparticles. The $CoFe_2O_4$/SBA-15/CuPc@Gd shows a surface area by BET and t-plot of 122.2 m^2/g and 86.28 m^2/g respectively, with a mean pore size of 5.37 nm, and pore volume of 0.164 cm^3/g. The catalyst was used for the synthesis of tetrazole in an aqueous medium. There is no reduction in the conversion of nitrile to tetrazole after the 5 cycles for $CoFe_2O_4$/SBA-15/CuPc@Gd. Also, the catalyst was used for the oxidation of sulfides to sulfoxide.
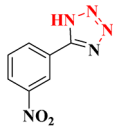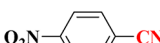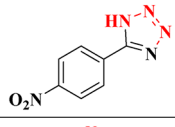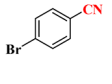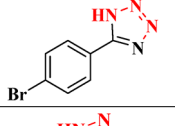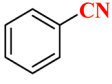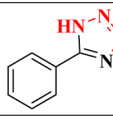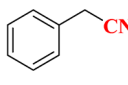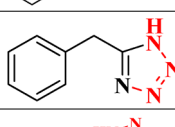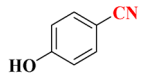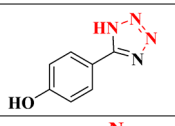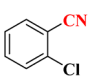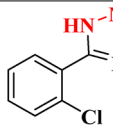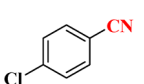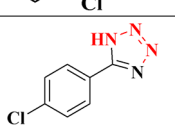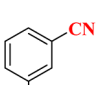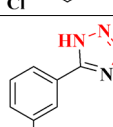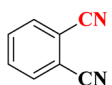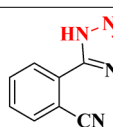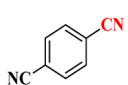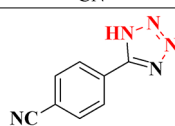
Entry	Substrate	Product	Time (min)	Yield (%)	TON[a]	TOF[b] (min⁻¹)	M. p (°C)
1	3-nitrobenzonitrile	tetrazole product	150	58	8.28	0.05	148–150 [93]
2	4-nitrobenzonitrile	tetrazole product	150	67	9.57	0.06	217–219 [93]
3	3-bromobenzonitrile	tetrazole product	90	55	7.85	0.09	182–184
4	4-bromobenzonitrile	tetrazole product	90	62	8.85	0.1	262–265 [131]
5	benzonitrile	tetrazole product	60	65	9.28	0.15	213–216 [93]
6	phenylacetonitrile	tetrazole product	120	58	8.28	0.07	122–125 [131]
7	4-hydroxybenzonitrile	tetrazole product	180	60	8.57	0.05	232–235 [132]
8	2-chlorobenzonitrile	tetrazole product	120	57	8.14	0.07	176–179 [93]
9	4-chlorobenzonitrile	tetrazole product	120	65	9.28	0.08	262–264 [93]
10	3-chlorobenzonitrile	tetrazole product	120	59	8.42	0.07	131–133 [131]
11	phthalonitrile	tetrazole product	50	78	11.14	0.56	210–212 [67]
12	terephthalonitrile	tetrazole product	45	80	11.43	0.25	250–253 [12]

Table 4. Synthesis of 5-substituted 1*H*-tetrazoles derivatives in the presence of $CoFe_2O_4$/SBA-15/CuPc@Gd. Reactions conditions: Nitrile (1 mmol), NaN_3 (1.2 mmol), H_2O (3 mL), and catalyst (100 mg). [a]TON, turnover number, moles of aryl halides converted per mole of Pd. [b]TOF, turnover frequencies, TON/time of reaction.
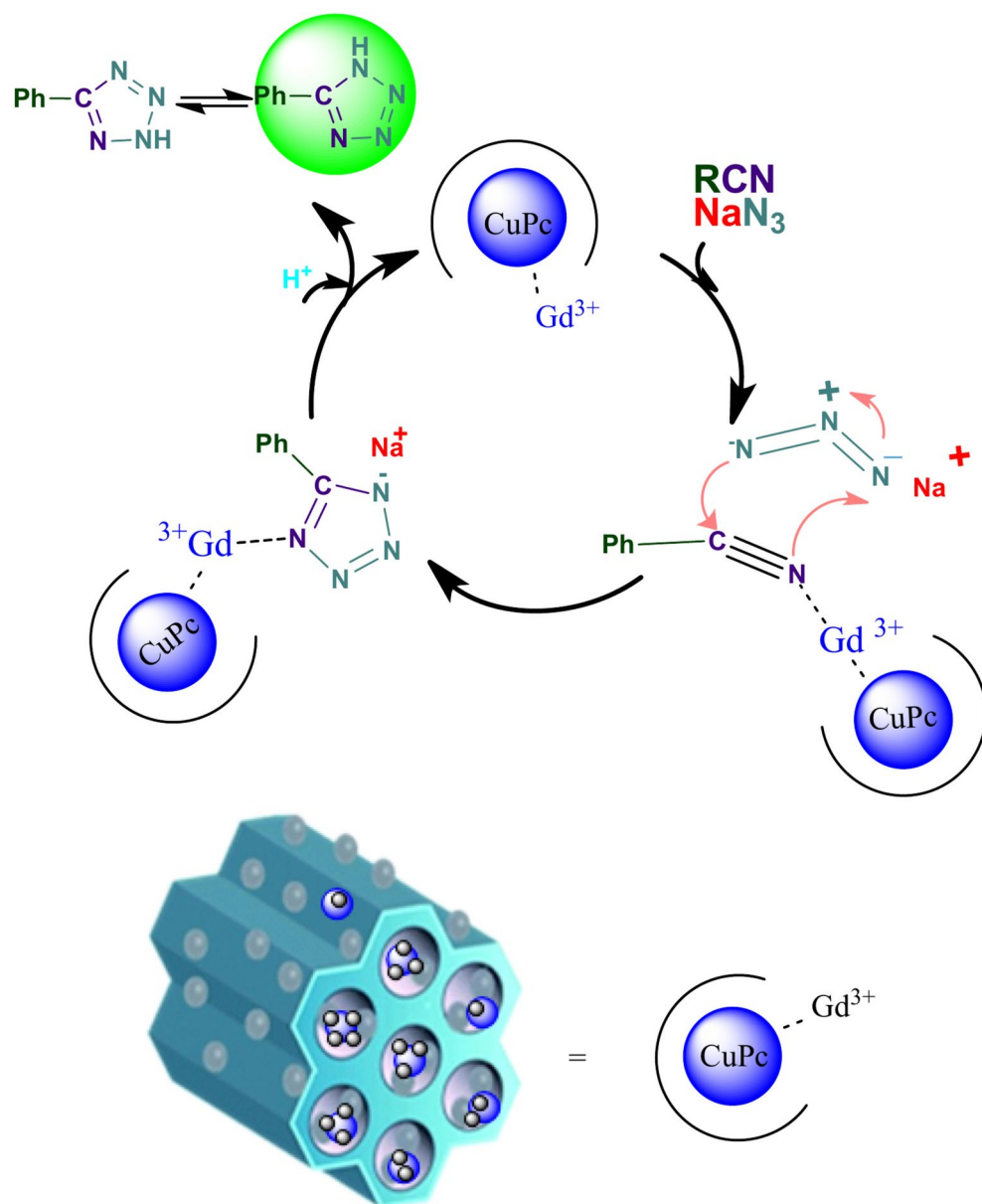
Scheme 1. Plausible Reaction Pathway for the Direct Conversion of over the CoFe$_2$O$_4$/SBA-15/CuPc@Gd Catalyst.

Entry	Solvent	Catalyst (mg)	H_2O_2 (mL)	Time (min)	Yield (%) [a]
1	Water	8	0.5	120	60
2	Ethyl acetate	8	0.5	120	35
3	ACN	8	0.5	120	45
4	EtOH	8	0.5	45	91
5	EtOH	10	0.5	45	93
6	EtOH	6	0.5	60	80
7	EtOH	4	0.5	120	78
8	EtOH	–	0.5	120	nil
9	EtOH	8	0.3	55	80
10	EtOH	8	0.1	70	50

Table 5. Optimization of reaction parameters for the synthesis sulfoxide. Reaction conditions: Sulfide (1 mmol), H_2O_2, catalyst, and solvent (3 mL). [a]Isolated yield.
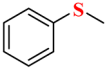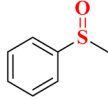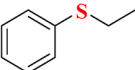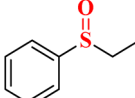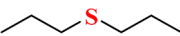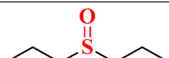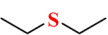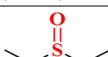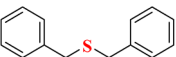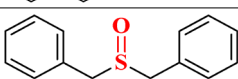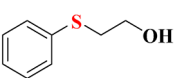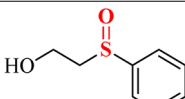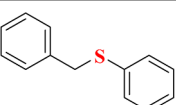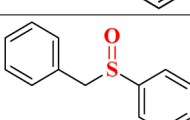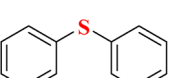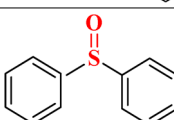
Entry	Substrate	Product	Time (min)	Yield (%)	TON	TOF	M. p (°C)
1			20	85	12.12	0.61	Oil [137]
2			45	89	12.70	0.28	Oil [138]
3			25	80	11.40	0.46	Oil [131]
4			20	88	12.54	0.63	Oil [131]
5			30	65	9.27	0.31	129–131 [139]
6			60	80	11.41	0.19	Oil [137]
7			25	75	10.70	0.43	116–118 [140]
8			30	65	9.27	0.31	63–65 [139]

Table 6. Synthesis of sulfoxides derivatives in the presence of CoFe$_2$O$_4$/SBA-15/CuPc@Gd. Reactions conditions: Sulfide (1 mmol), catalyst (5 mg), and H_2O_2 (0.5 mL) as oxidant at room temperature.
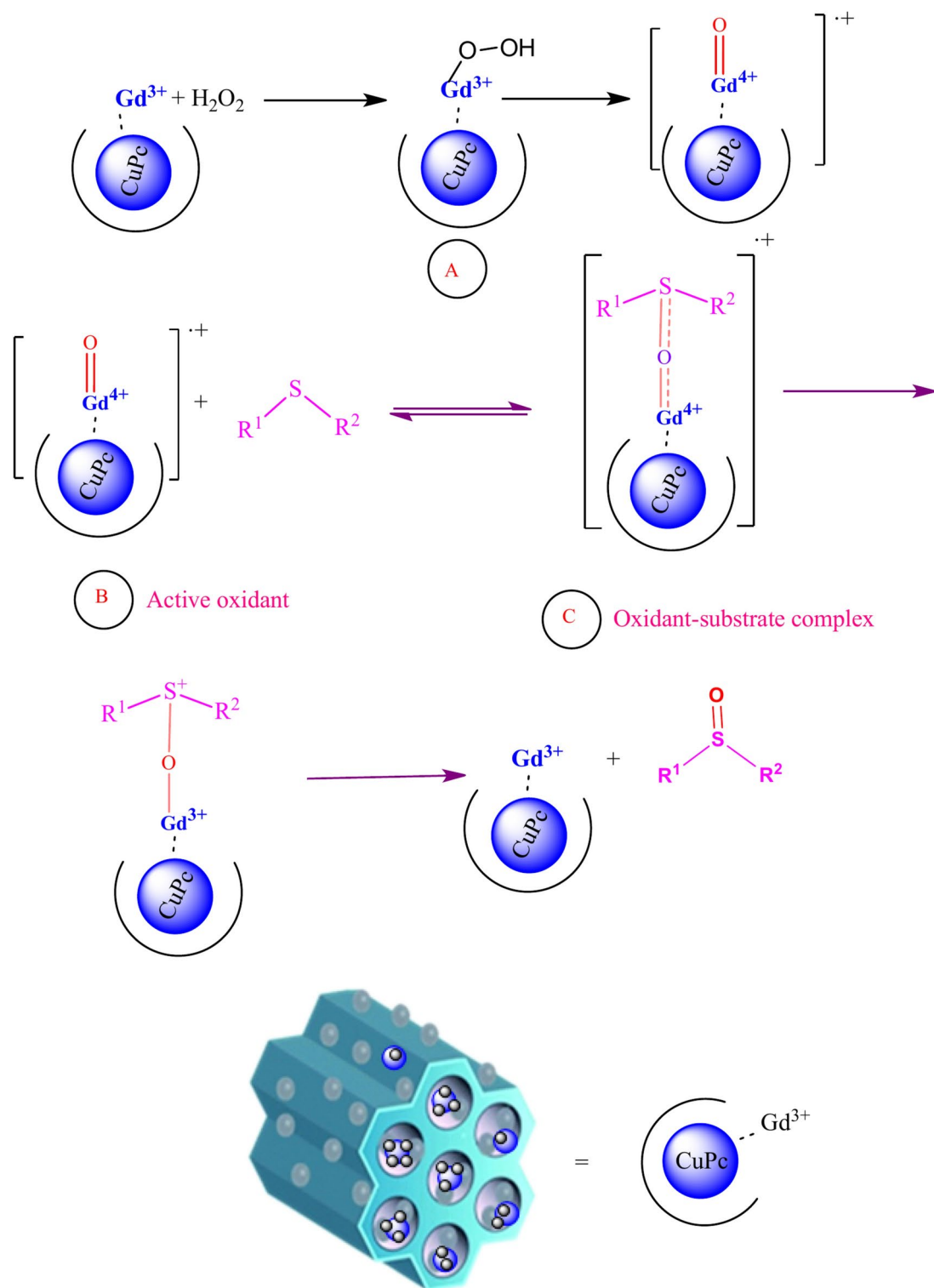
Scheme 2. Oxygen atom transfer mechanism for the selective oxidation of sulfides to sulfoxide.
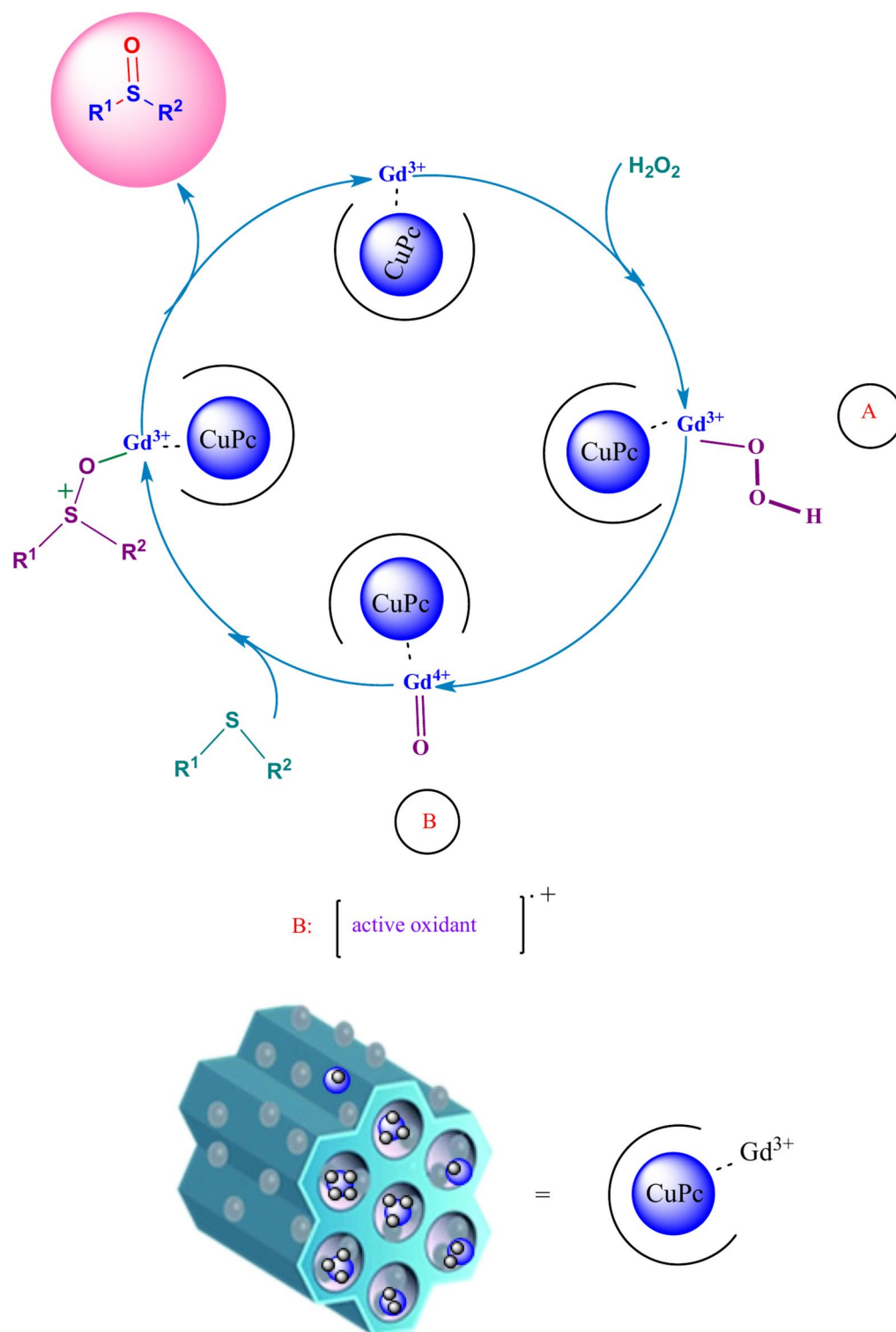
Scheme 3. A plausible mechanism for sulfoxide formation reactions using H_2O_2 over $CoFe_2O_4$/SBA-15/ CuPc@Gd catalyst.
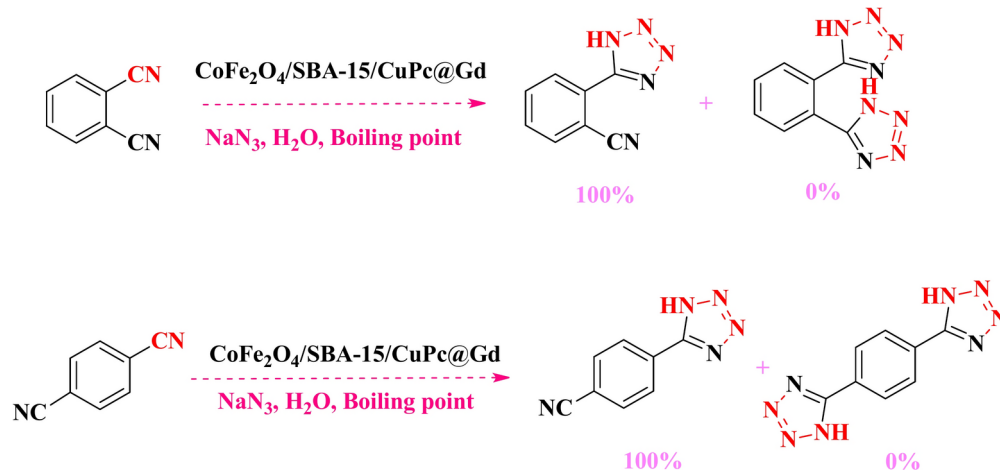
Scheme 4. Homoselectivity of CoFe$_2$O$_4$/SBA-15/CuPc@Gd in the synthesis of tetrazoles.
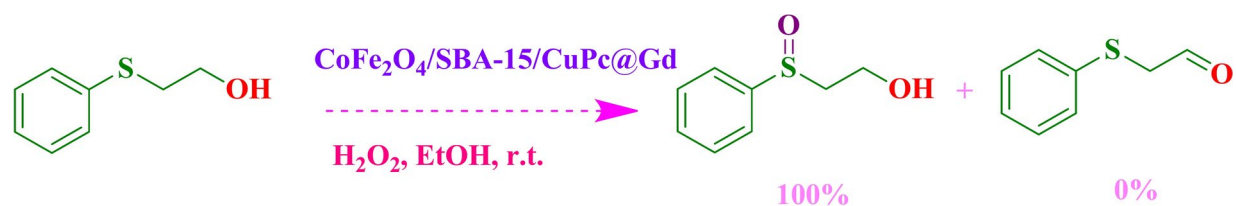
Scheme 5. Chemoselective sulfoxidation of 2-(phenylthio) ethanol.
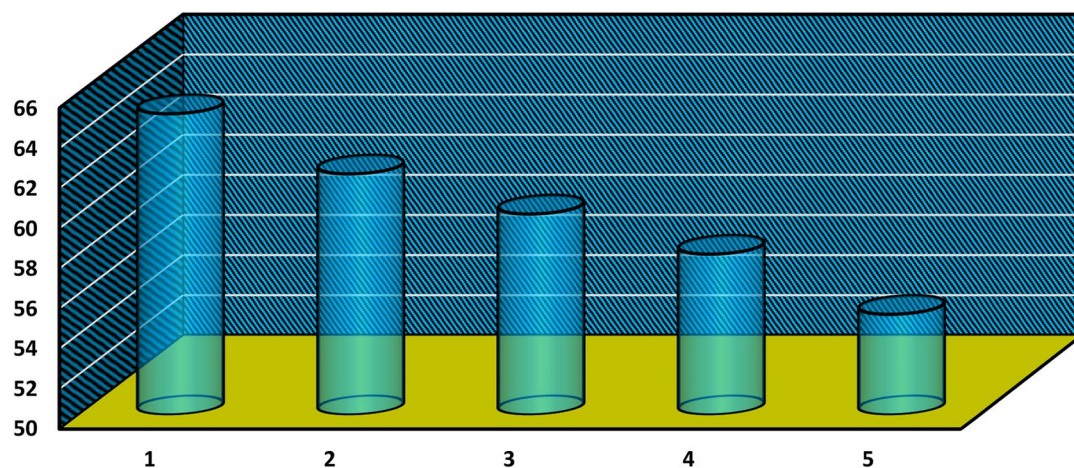
Fig. 11. Reusability of the CoFe$_2$O$_4$/SBA-15/CuPc@Gd.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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Author contributions

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Declarations

Competing interests
The authors declare no competing interests.

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