One-, two- and three-dimensional coordination polymers based on copper paddle-wheel SBUs as selective catalysts for benzyl alcohol oxidation

Leila Asgharnejad, Alireza Abbasi, Mahnaz Najafi, Jan Janczak

PII: S0022-4596(19)30298-1

DOI: https://doi.org/10.1016/j.jssc.2019.06.011

Reference: YJSSC 20806

To appear in: *Journal of Solid State Chemistry*

Received Date: 26 January 2019

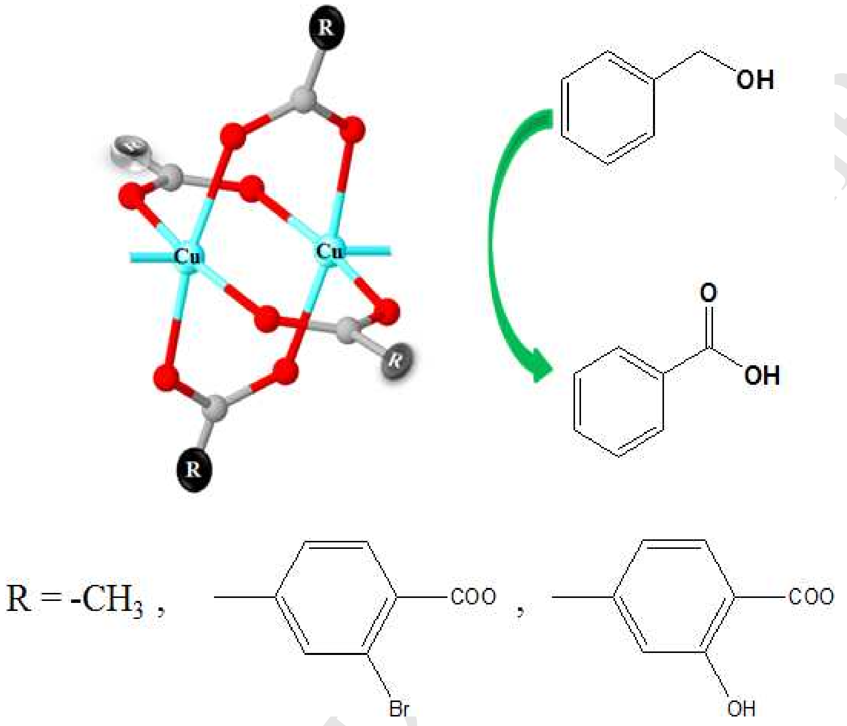
Revised Date: 24 April 2019

Accepted Date: 5 June 2019

Please cite this article as: L. Asgharnejad, A. Abbasi, M. Najafi, J. Janczak, One-, two- and three-dimensional coordination polymers based on copper paddle-wheel SBUs as selective catalysts for benzyl alcohol oxidation, *Journal of Solid State Chemistry* (2019), doi: https://doi.org/10.1016/j.jssc.2019.06.011.

Graphical abstract:

Cu(II)-coordination polymers with binuclear paddle-wheel SBUs as heterogeneous catalysts for benzyl alcohol oxidation



One-, two- and three-dimensional coordination polymers based on copper paddle-wheel SBUs as selective catalysts for benzyl alcohol oxidation

Leila Asgharnejad[a], Alireza Abbasi[b*], Mahnaz Najafi[b] and Jan Janczak[c]

[a]School of Chemistry, Alborz Campus, University of Tehran, Tehran, Iran.

[b]School of Chemistry, College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran.

E-mail: aabbasi@khayam.ut.ac.ir.

[c]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland.

Abstract

Copper-based coordination polymers, $Cu_2(\mu_2\text{-}MeCO_2)_4(DABCO)$ (**1**), [Cu(1,4-BDC-Br)$(DABCO)_{0.5}$].xDMF.yH_2O (**2**) and Cu(1,4-BDC-OH)(DMF) (**3**) (1,4-BDC-Br = 2-bromoterephthalate, DABCO = triethylenediamine, 1,4-BDC-OH = 2-hydroxyterephthalate) were solvothermally synthesized. Two polymorphs of **1** (**1a** and **1b**) were obtained which both contain 1-D chains with similar connectivity and different packing. Compound **2** is a 3-D metal-organic framework (MOF) and **3** exhibits a 2-D structure. Structural analyses of the coordination polymers showed that they all have similar paddle-wheel secondary building units (SBUs). The coordination polymers **1**-**3** were characterized by FT-IR, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and atomic absorption spectroscopy. Compound **2** is further analyzed by nitrogen adsorption/desorption techniques. The obtained coordination compounds were employed as heterogeneous catalysts for selective oxidation of benzyl alcohol to benzoic acid using CH_2Cl_2 as solvent and *tert*-butyl hydroperoxide (TBHP) as oxidant. The catalysts displayed good activity in the oxidation reaction and could be reused without noticeable loss of activity.

Keywords: Cu-coordination polymers, crystal structure, selective catalysts, benzyl alcohol oxidation

1. Introduction

Selective oxidation of alcohols to aldehyde, ketone or acid products is a pivotal transformation in fine chemicals and pharmaceutical industries. Catalytic oxidation systems have been focused from industrial and academic views. [1, 2] Traditionally, stoichiometric amounts of oxidizing agents (e.g. MnO_2, CrO_3, $K_2Cr_2O_7$, SeO_2, etc) have been utilized under harsh reaction industrial conditions which caused environmental issues and increased production costs. Therefore, development of active and selective catalytic systems is a continuing demand for economic and sustainable chemical transformations. [1, 3]

There are some reports about development of catalysts based on supported noble metals such as Au,[4] Pd,[5] Ru[6] or a combination of them.[7] However, these catalysts are expensive and suffer from sustainable points of views.[8] Transition metal-based catalysts were also immobilized using supports including graphene oxide,[9] polymers,[10] metal nanoparticles[11] and silica.[12] For instance, there have been many reports on the catalytic oxidation of alcohols over supported Cu(II) complexes.[13-16]

Coordination polymers and metal-organic frameworks (MOFs), with adjustable molecular structures and electronic properties, offer a plentiful supply of transition metals with catalytic characteristics. These materials are inorganic-organic hybrids assembled from metal ions or clusters which are held by organic linkers. [17, 18] Unique features of these crystalline compounds such as uniform arrangement of catalytic sites with high concentration, stable architecture and reusability make them suitable candidates in the field of heterogeneous catalysis. [19-21]

Copper (II)-coordination polymers and MOFs have been already proved to be promising catalysts for alcohol oxidation.[22-26] In this regard, we previously reported copper molybdate $[CuMoO_4(1,10\text{-Phen})].H_2O$ (Phen = 1,10-phenanthroline) coordination polymer and $Cu_3(BTC)_2$ MOF (BTC = 1,3,5-tricarboxylate) as heterogeneous catalysts for epoxidation of allylic alcohols. [27, 28] Recently, Rajeev Gupta’s group synthesized Cu(II)-coordination polymers containing metalloligands and applied them as heterogeneous catalysts for the oxidation of benzyl alcohol. [29] Catalytic oxidation of benzyl alcohol was also reported over other Cu(II)-based MOFs and coordination polymers such as $Cu(1,4\text{-BDC})(DABCO)_{0.5}$ (1,4-BDC = terephthalic acid) [30] and $Cu_3(BTC)_2$ [23], $\{[Cu(fcz)_2(H_2O)].SO_4.DMF.2CH_3OH\cdot 2H_2O\}_n$ and $\{[Cu(fcz)_2Cl_2].2CH_3OH\}_n$ (fcz = 1-(2,4 difluorophenyl)-1,1-bis[(1H-1,2,4-triazol-l-yl)methyl]ethanol).[22]

Herein, we report solvothermal self-assembly synthesis and structural features of new 1-D, 2-D and 3-D coordination polymers based on Cu(II) paddle-wheel SBUs including $Cu_2(\mu_2\text{-}MeCO_2)_4(DABCO)$ (**1**), $[Cu(1,4\text{-BDC-Br})(DABCO)_{0.5}].xDMF.yH_2O$ (**2**) and Cu(1,4-BDC-OH)(DMF) (**3**). The prepared coordination polymers were applied as heterogeneous catalysts for oxidation of benzyl alcohol.

2. Experimental

2.1. Materials and characterization

All reagents were purchased from commercial sources and used without further purification.

FT-IR spectra were acquired by means of a Bruker Equinox 55 spectrometer equipped with a single reflection diamond ATR system. Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'Pert PRO instrument using Cu K_α radiation (λ = 1.5406 Å). Thermogravimetric analysis (TGA) was measured in N_2 atmosphere using Dupont 951 Thermogravimetric Analyzer. The surface area and pore volume of MOF **2** were identified by nitrogen adsorption/desorption measurements at liquid nitrogen temperature utilizing BELSORP-mini II instrument. The sample was degassed under vacuum at 130 °C for 4 h before the experiments. The oxidation products were determined using a gas chromatograph (HP, Agilent 5890) equipped with a capillary column (HP-1) and a flame ionization detector (FID). The copper content in the catalysts was measured by AA-400 atomic absorption spectrometer.

2.2. Synthesis of 1a and 2

A mixture of $Cu(NO_3)_2.3H_2O$ (0.06 g, 0.25 mmol), DABCO (0.07 g, 0.62 mmol), 1,4-BDC-Br (0.044 g, 0.18 mmol) and CH_3COOH (0.08 mL) was dissolved in DMF (5 mL) and then stirred for 10 min. The suspension was transferred into a Teflon-lined autoclave and kept at 110 ºC for 24 h to afford a mixture of **1a** and **2**. Green parallelepiped crystals of **1a** were settled at the bottom of the vessel and the above solution containing small crystals of **2** were isolated by decantation. Crystals of **1a** and **2** were washed with fresh DMF and dried in air.

2.3. Synthesis of 1b

Coordination polymer **1b** was synthesized by solvothermal reaction of $Cu(NO_3)_2.3H_2O$ (0.016 g, 0.07 mmol), DABCO (0.056 g, 0.5 mmol) and CH_3COOH (0.08 mL) in DMF (5 mL). After stirring of the reagents for 10 min, the mixture was placed into a Teflon-lined autoclave and kept at 120 ºC for 24 h. Blue parallelepiped crystals of **1b** were separated by filtration, washed with DMF and then dried in air.

2.4. Synthesis of 3

The 1,4-BDC-OH ligand was synthesized according to previous method reported in the literature.[31] To synthesize coordination polymer **3**, $Cu(NO_3)_2.3H_2O$ (0.08 g, 0.33 mmol) and 1,4-BDC-OH (0.046 g, 0.25 mmol) were added to a mixture of DMF (4 mL) and EtOH (1 mL) in a 25 mL Teflon container and then stirred for 10 min at room conditions. The mixture was kept in a stainless-steel autoclave at 80 ºC for 24 h. After slow cooling of the vessel to room temperature, green crystals of **3** were collected and washed with DMF.

2.5. Catalytic procedure

The oxidation of benzyl alcohol was carried out as follows: A mixture containing *tert*-butyl hydroperoxide (TBHP, 2.26 mmol), benzyl alcohol (1 mmol) and catalyst (0.063 mmol based on Cu) in solvent (1 mL) was prepared. TBHP (70% in H_2O) was dried prior to use based on the procedure reported in the literature using CH_2Cl_2.[32] The mixture was stirred for proper time either at room temperature or at 40 ºC and then the oxidation products were analyzed by GC.

2.6. X-ray single crystal data collection and refinement

Single-crystal structure analyses were carried out on a four-circle κ geometry KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector using graphite-monochromated Mo K_α radiation. The structures were solved by the direct method using SHELXS-97 and refined using SHELXL-2014/7 program.[33] All non-hydrogen atoms were refined anisotropically. The CCDC numbers are 1571179 (**1a**), 1571178 (**1b**) and 1860730 (**3**).

3. Result and Discussion

3.1 Crystal structures

3.1.1. Structure of $Cu_2(\mu_2\text{-}MeCO_2)_4(DABCO)$ (**1a**)

Crystallographic data of the structures are given in Table 1. The ORTEP diagram of **1a** is illustrated in Fig. 1a. Two Cu^{2+} ions, one DABCO molecule and four μ_2-$MeCO_2$ ligands exist in the asymmetric unit of this structure. There are two crystallographically distinct Cu^{2+} ions which are joined through linear DABCO ligand. Square pyramidal configuration around each Cu^{2+} center contains one N atom from a DABCO molecule in the axial site (Cu1-N1, 2.195(3); Cu2-N2, 2.196(3) Å) and four O atoms from four different μ_2-$MeCO_2$ ions. The Cu1-O and Cu2-O bond lengths are within the range of 1.966(2)-1.984(2) and 1.972(2)-1.989(2) Å, respectively (Table S1).

The Cu^{2+} ions are further joined each other via bridging DABCO and μ_2-$MeCO_2$ ligands to form the 1-D chain depicted in Fig 1b. The Cu1 …. Cu1 and Cu2 …. Cu2 distances within $\{Cu_2(\mu_2\text{-}MeCO_2)_4\}$ units are 2.6155(8) and 2.6142(8) Å, respectively. Some hydrogen bonding interactions are observed between H atoms of DABCO and O atoms of μ_2-$MeCO_2$ ligands in the chains (Table S2). In this structure, the chains grow along two different directions which led to the packing exhibited in Fig 1c. The PXRD pattern of **1a**, presented in Fig. 2a, is similar to that of the simulated pattern, indicating the purity of the sample.

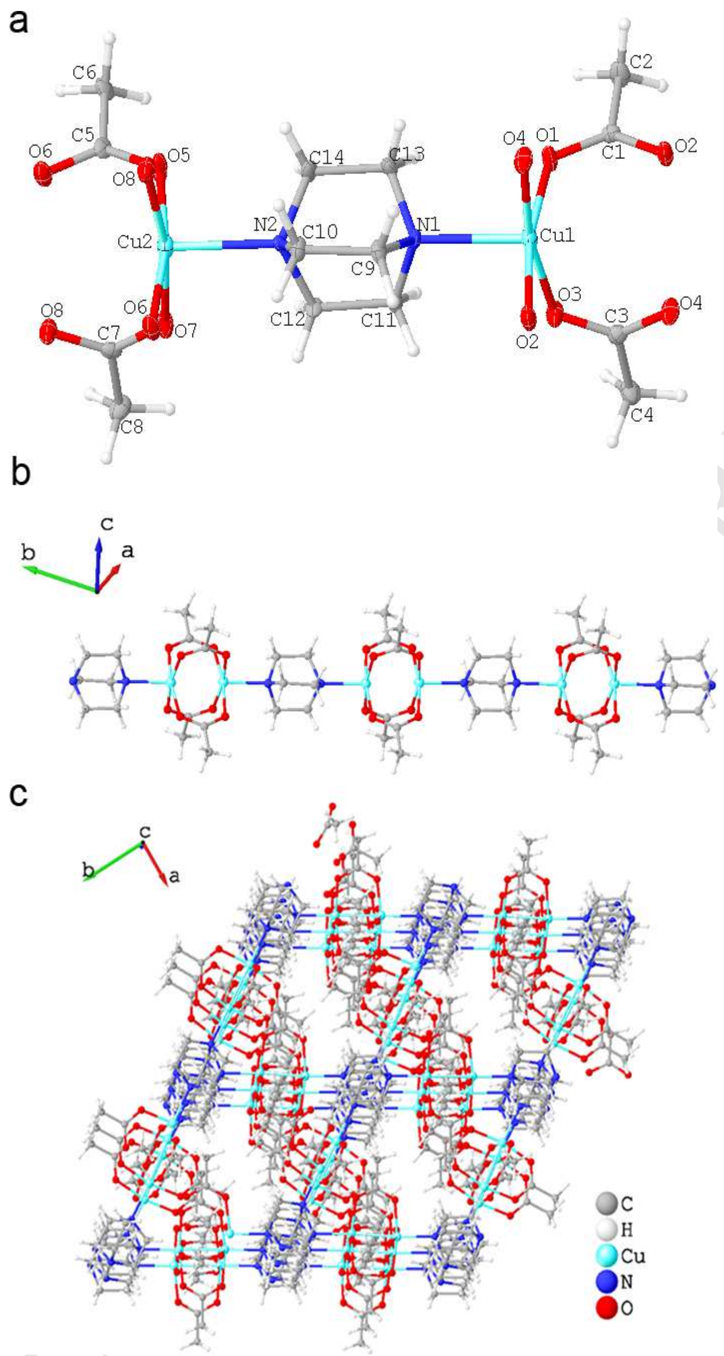


Fig. 1 a) ORTEP, b) 1-D chain and c) packing of **1a**

Table 1 Crystal structure and data refinement for **1a**, **1b** and **3**

Compound	**1a**	**1b**	**3**
Empirical formula	$C_{14}H_{24}Cu_2N_2O_8$	$C_{14}H_{18}Cu_2N_2O_8$	$C_{11}H_{11}CuNO_6$
Molecular weight	475.43	469.40	316.75
Temperature (K)	100(2)	100(2)	100(2)
Wavelength, Mo Kα (Å)	0.71073	0.71073	0.71073
Space group	*P*21/*c*	*C*2/m	*I*2/m
a (Å)	10.1816(8)	8.0473(5)	7.6618(4)
b(Å)	16.239(2)	15.3181(8)	15.3855(7)
c (Å)	11.6419(9)	7.6289(4)	11.0185(7)
α (°)	90	90	90
β (°)	97.660(10)	104.346(8)	107.978(7)
γ (°)	90	90	90
Cell volume ($Å^3$)	1907.7(3)	911.08(9)	1235.45(13)
Z	4	2	4
ρ ($g\ cm^{-3}$)	1.655	1.704	1.703
μ (mm^{-1})	2.272	2.377	1.790
Total reflections	38375	5275	11410
Unique reflections	4988	1202	1668
Observed reflections [$F^2 > 2\sigma(F^2)$]	3003	1066	1315
R_{int}	0.0650	0.0364	0.0672
Data/restraints/parameters	4988/0/239	1202/3/84	1668/0/110
Goodness-of-fit (GOF) on F^2	1.005	1.003	1.002
R [$F^2 > 2\sigma(F^2)$] (R_1, wR_2)	0.0425, 0.0683	0.0328, 0.0729	0.0502, 0.0936
R (all data) (R_1, wR_2)	0.0915, 0.0758	0.0400, 0.0755	0.0752, 0.1026
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.410, -0.413	0.612, -0.469	0.616, -0.699

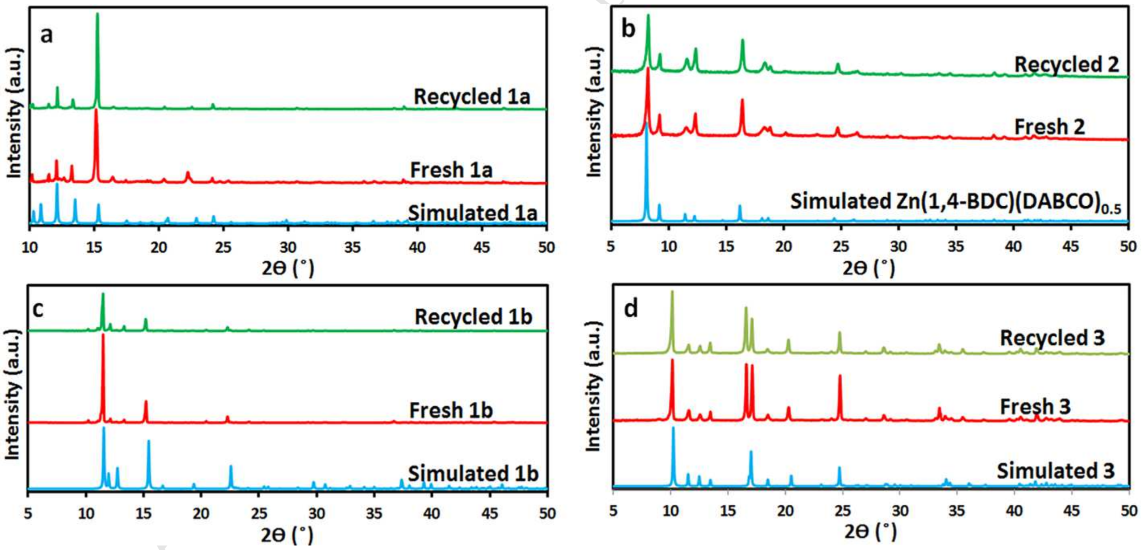


Fig. 2. XRD patterns of **1-3**

3.1.2. Structure of [Cu(1,4-BDC-Br)$(DABCO)_{0.5}$].xDMF.yH_2O (**2**)

Since our effort for obtaining crystals suitable for structure determination by single-crystal X-ray diffraction resulted in failure, phase and purity of this compound were studied using PXRD. The pattern of **2** is similar to that of [Zn(1,4-BDC)$(DABCO)_{0.5}$] MOF previously reported by Danil N. Dybtsev *et al.*,[34] confirming that these two compounds are isostructural and the structure of the MOF is not affected by functionalization of 1,4-BDC (Fig. 2b). The molecular structure and 3D packing of [Zn(1,4-BDC)(DABCO)$_{0.5}$] MOF are shown in Fig. 3. The MOF contains binuclear-paddle wheel units bridged by 1,4-BDC and form 2D layers which are further connected by pillared DABCO ligands.

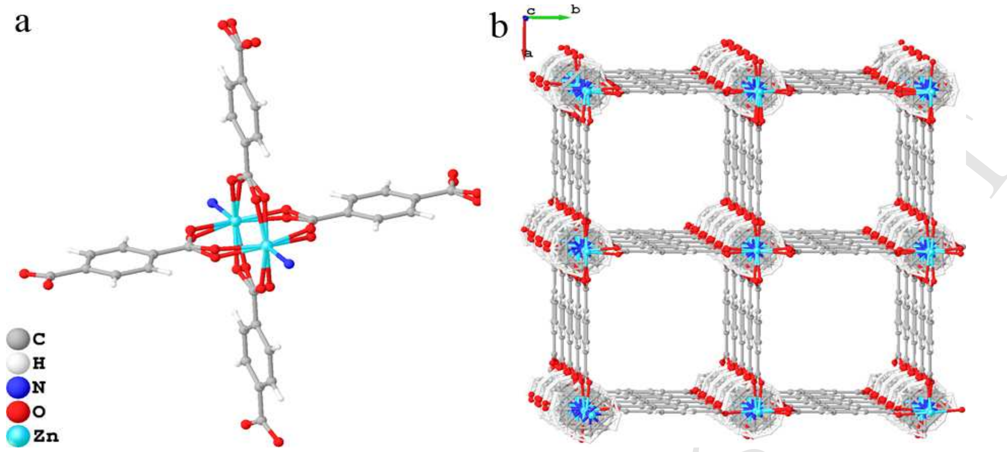


Fig. 3. a) Paddle-wheel and b) 3-D structure of [Zn(1,4-BDC)(DABCO)$_{0.5}$][34]

3.1.3. Structure of $Cu_2(\mu_2\text{-}MeCO_2)_4$(DABCO) (**1b**)

This structure is a polymorph of **1a**. The molecular structure of binuclear **1b** is shown in Fig. 4a. The asymmetric unit of **1b** is composed of one Cu^{2+} ion, one μ_2-$MeCO_2$ ion and half of a DABCO molecule. There is one crystallographically distinct Cu^{2+} ion which is coordinated to N atom of a DABCO molecule in the axial site. The carbon atoms of DABCO are disordered. The structure of **1b** showed similar connectivity to that of **1a** and Cu^{2+} centres are five-coordinated by N from DABCO ligand (Cu1-N1, 2.205(2) Å) and four O atoms from μ_2-$MeCO_2$ molecules with the Cu1-O bond lengths of 1.9684(16) and 1.9732(17) Å (Table S3).

The binuclear units are joined together through linear DABCO molecules and form 1-D chain seen in Fig. 4b. The Cu …. Cu distance in the chain is 2.632(6) Å which is slightly longer compared to those in **1a**. Unlike **1a**, the chains in **1b** are all aligned in a similar direction to afford the packing demonstrated in Fig. 4c.

Similar paddle wheel units were reported in some MOFs synthesized based on DABCO and 1,4-BDC or functionalized 1,4-BDC including [Co_2(1,4-BDC)$_2$(DABCO)].4DMF.H_2O,[31, 35] [Ni_2(1,4-BDC)$_2$(DABCO)].4DMF.H_2O,[36] [Cu_2(1,4-BDC-NH_2)$_2$(DABCO)].2DMF.2H_2O (1,4-BDC-NH_2 = 2-aminoterephthalate)[37] and [Zn_2(1,4-BDC-OH)$_2$(DABCO)$_{0.5}$].1.5DMF.0.3H_2O.[31] Acetate ions as monotopic carboxylate ligands in **1a** and **1b** afforded the formation of 1-D chains while the ditopic functionalized 1,4-BDC ligands in **2** as well as the previously reported structures mentioned above led to the formation of 3-D MOFs. Although 1,4-BDC-Br, DABCO and acetic acid were utilized in the solvothermal synthesis of **1a**, the 1,4-BDC-Br does not appear in this structure and we obtained a mixture containing coordination polymer **1a** and MOF **2**. To investigate how 1,4-BDC-Br affects the final products, the synthesis was carried out under similar conditions to those mentioned above, except that 1,4-BDC-Br was omitted. Rod-shape crystals were formed which were not suitable for X-ray single crystal analysis. However, the PXRD pattern of these crystals is not similar to that of **1a** (Fig. S1). Thus, we made an attempt to obtain better crystals for X-ray analysis by changing the reaction conditions such as molar ratio of the starting materials and the reaction temperature and this resulted in compound **1b**.

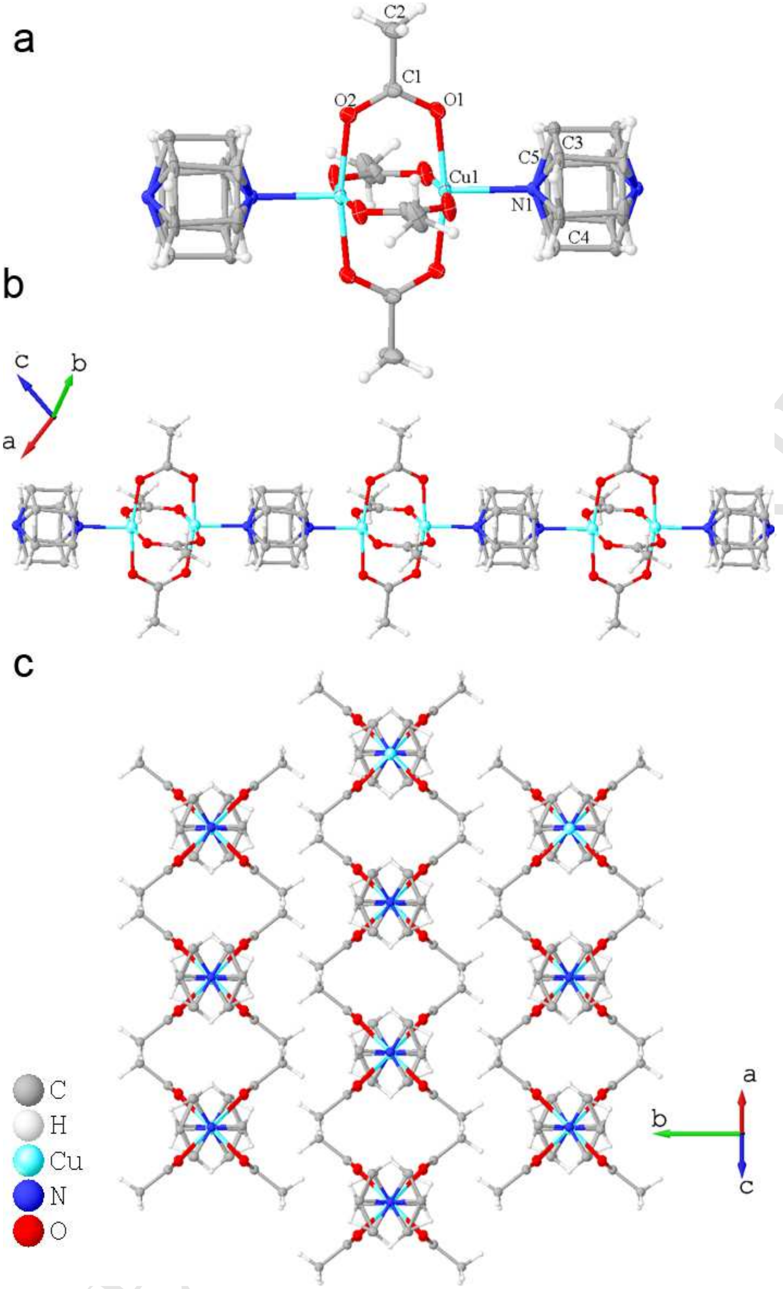


Fig. 4. a) ORTEP, b) 1-D chain and c) packing of **1b**

3.1.4. Structure of Cu(1,4-BDC-OH)(DMF) (**3**)

The ORTEP view of coordination polymer **3** is displayed in Fig. 5a. The asymmetric unit in this structure is composed of one Cu^{2+} ion, half of a 1,4-BDC-OH and one DMF molecule. The OH groups of 1,4-BDC-OH ligand occupies two positions (both with the occupancy of 0.5). The DMF molecules have also two orientations (occupancy of 0.5 for each) with two common atoms (O4 and C6). Each Cu^{2+} ion exhibits a square pyramidal configuration and is coordinated to four O atoms from four 1,4-BDC-OH ligands (Cu-O1, 1.948(2) Å; Cu-O2^{i}, 1.971(2) Å; Cu-O2^{ii}, 1.971(2) Å; Cu-O1^{iii}, 1.948(2) Å (symmetry codes: (i) 2-x, y, 1-z; (ii) 2-x, 1-y, 1-z; (iii) x, 1-y, z) and one O atom of a DMF molecule in the axial position (Cu-O4, 2.135(4) Å). The bond lengths and angles for **3**, shown in Table S4, lie within the range of those reported for similar paddle-wheel structures.[38]

The paddle-wheel units with Cu….Cu distances of 2.642 Å, are connected through the carboxylate groups of 1,4-BDC-OH ligand to form a 2D layer shown in Fig 5b.

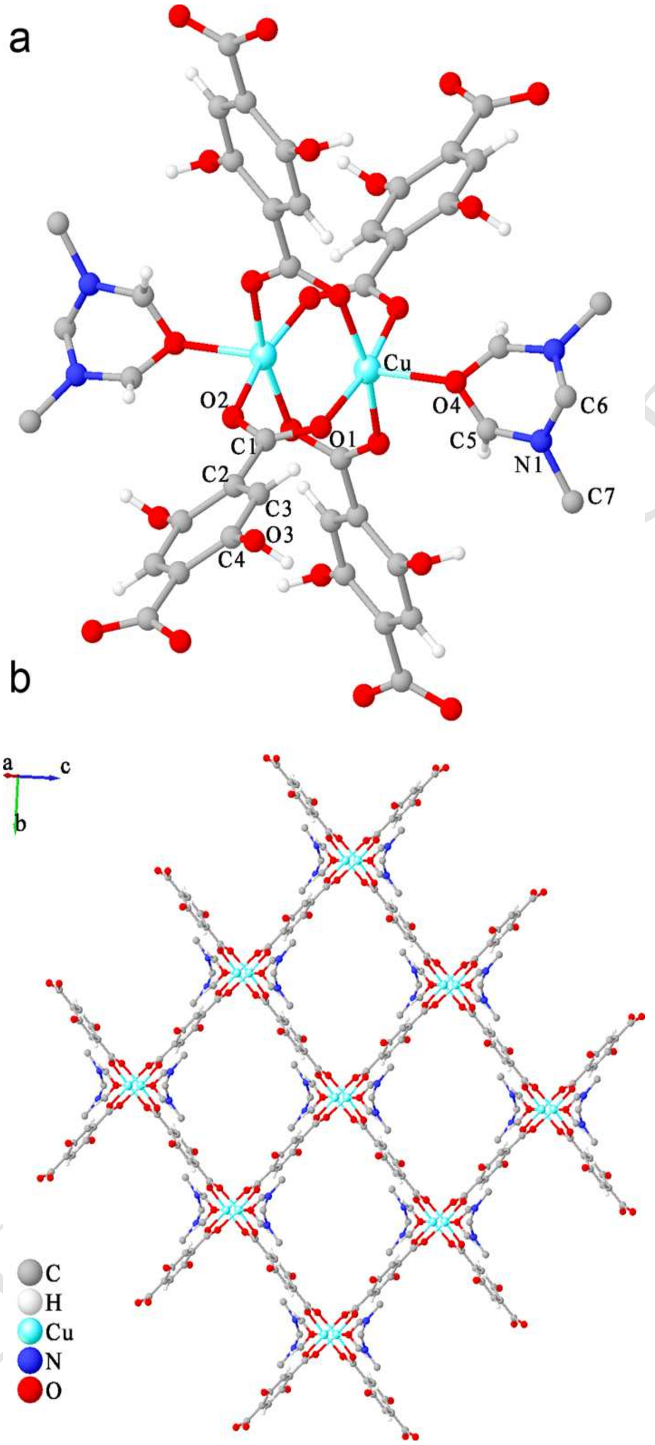


Fig. 5. a) ORTEP, b) 2-D chain structure of **3**

3.2. Spectroscopic analysis

The FT-IR spectra of **1**-**3** are presented in Fig. 6. In the FT-IR spectra of fresh **1a** and **1b**, the symmetric and asymmetric vibrations of COO groups for μ_2-$MeCO_2$ ligand are observed at 1417 and 1612 cm^{-1}, respectively.[39] The ν (C-N) of DABCO ligand is seen at 1060 cm^{-1}. In the FT-IR spectrum of MOF **2**, ν_{as} (C-N) and ν_s (C-N) for DABCO appeared at 1089 and 1058 cm^{-1}, respectively. Moreover, the bands located at 1623 and 1672 cm^{-1} are ascribed to the ν_{as} (COO) vibrations of 1,4-BDC-Br ligand. The peak at 1383 cm^{-1} can be assigned to ν_s (COO) of this ligand.[36, 40, 41] Similar to **2**, the FT-IR spectra of **3** exhibited the bands for ν (COO) vibrations exist in the structure of 1,4-BDC-OH ligand.

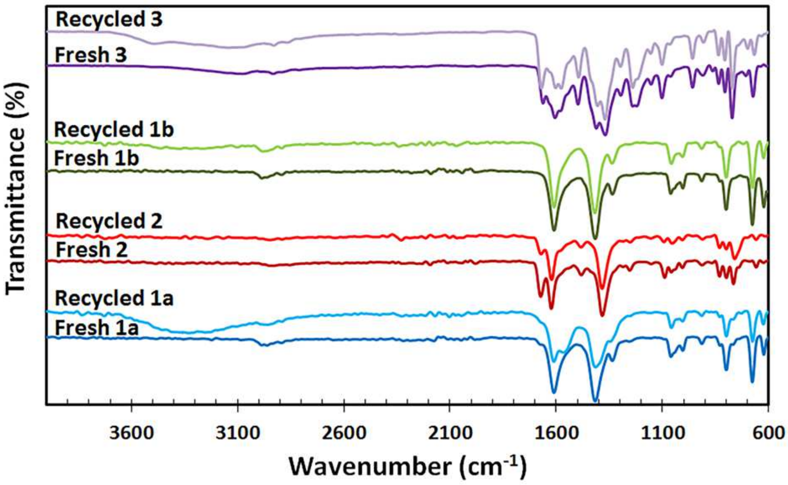


Fig. 6. FT-IR spectra of **1-3**

3.3. Thermal stability

Thermogravimetric analyses were conducted to evaluate thermal stability of **1**-**3** as shown in Fig. 7. In coordination polymer **1a**, the weight loss of approximately 4 % up to 190 ºC is probably due to adsorbed solvent molecules (DMF and/or H_2O). One distinct weight loss step occurred upon heating to 300 ºC owing to the decomposition of organic ligands. The residue of about 34 % (calculated 33.46 %) is attributed to copper oxide. In the TGA curve of MOF **2**, the weight loss observed up to 230 ºC is related to the solvent molecules occupying the pores of the MOF. Then the guest-free framework of **2** decomposes up to 510 ºC due to the elimination of organic molecules. Coordination polymer **1b** is stable up to 170 ºC, followed by a one-step weight loss by increasing in the temperature to 270 ºC, which is attributed to the removal of organic molecules. TG curve of **3** exhibits no weight loss till 210 ºC and then is decomposed in two steps. The first weight loss of 22.66 % (calculated 23 %) observed at 210-280 ºC can be due to one DMF molecule. The residue of 24.99 % (calculated 25.11 %) at 600 ºC is related to copper oxide. Powder XRD analyses for **1-3** after annealing at 600 ºC confirm that the residue is CuO (Fig. S2-S5).

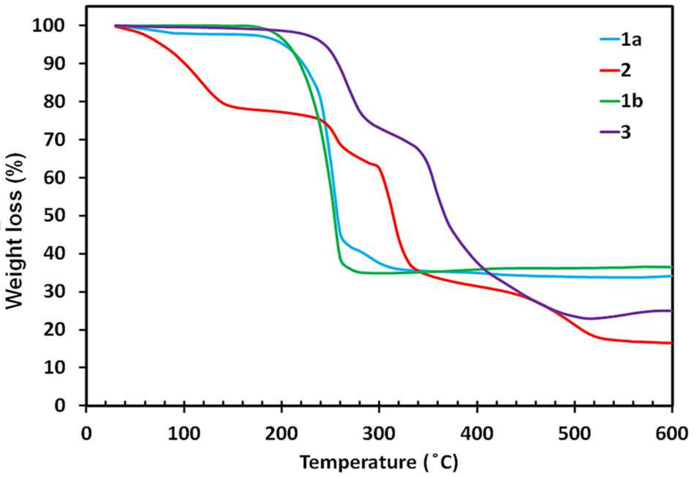


Fig. 7. TGA curves of **1-3**

3.4. Textural analysis

The N_2 adsorption/desorption isotherm and pore size distribution of MOF **2** are shown in Fig. 8. The BET and Langmuir surface areas are estimated to be 1106 and 1211 m^2g^{-1}, respectively. Functionalization of 1,4-BDC by Br groups in MOF **2** provides a lower surface area compared to similar structures containing non-functionalized 1,4-BDC.[42] Moreover, pore diameter and pore volume for **2**, determined by MP (Micropore analysis) method are found to be 0.6 nm and 0.454 cm^3g^{-1}, respectively.

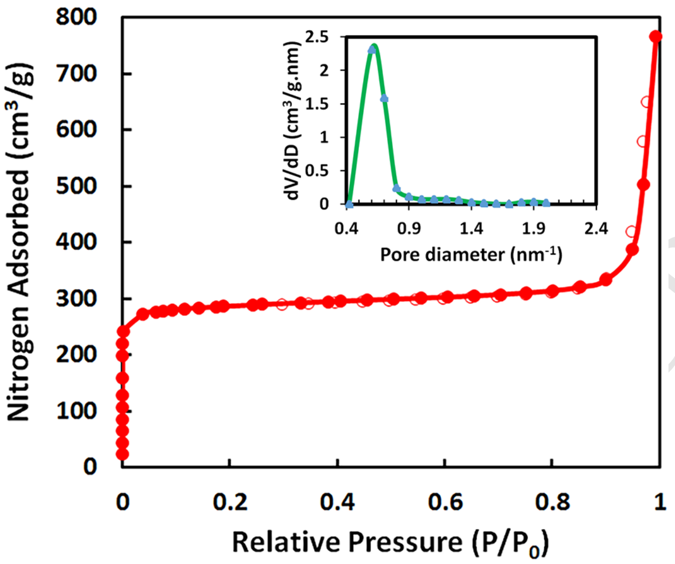


Fig. 8. Nitrogen sorption isotherm of MOF **2**

3.5. Catalytic tests

The catalytic performance of the prepared Cu-based coordination polymers was studied in the oxidation of benzyl alcohol using TBHP as oxidant. All four Cu-coordination polymers exhibited good catalytic activity and displayed selectivity towards the formation of benzoic acid at 40 ºC using CH_2Cl_2 as solvent.

Different factors such as solvent, temperature, time, *etc* can influence catalytic oxidation of organic substrates.[43, 44] Therefore, we have studies the effect of some parameters to obtain the optimal reaction conditions for benzyl alcohol oxidation in the presence of **1**-**3**. The results are summarized in Table 2 and 3.

At first, the oxidation was investigated in CH_2Cl_2 at room temperature. Catalysts **1a**, **2** and **3** selectively oxidized benzyl alcohol to benzaldehyde while a very small amount of benzoic acid was also formed when **1b** used as catalyst (Table 2, Entry 1-4). Since conversion of these reactions was 17-23 %, the reaction time was extended to 8 h (Table 2, Entry 5-8) to improve the conversion. The results show that the reaction conversion for all catalysts was not significantly improved upon time extension (23-28 %) although they were all still selective towards the formation of benzaldehyde.

To obtain optimal reaction conditions with good conversion and selectivity, DMF is used instead of CH_2Cl_2. Considering polarity of the solvents, DMF with dipole moment of 3.86 D can facilitate solubility of both TBHP and benzyl alcohol compared to CH_2Cl_2, which has dipole moment of 1.6 D.[44] The oxidation reactions were performed in DMF for 4 h using the catalysts. The results revealed that reaction conversions were improved to 30-54 % after 4 h for all catalysts and benzaldehyde and benzyl benzoate were formed as the products (Table 2, Entry 9-12). By increasing the time of the reactions to 12 h using DMF, conversions increased to 58-62 % while selectivity to benzaldehyde decreased (Table 2, Entry 13-16).

Since all four catalysts displayed selectivity to benzaldehyde in CH_2Cl_2, this solvent was selected for further study of benzyl alcohol oxidation. The reactions were conducted at 40 ºC to obtain better results (Table 3). As seen, the conversion of the oxidation reaction is above 82 % for **1a**, **1b** and **2** after 8 h. In the presence of catalyst **3**, the reaction led to 97 % conversion after 14 h. All catalysts in this condition afforded benzoic acid as the main product.

Table 2[a] Catalytic activity of coordination polymers **1-3** in the oxidation of benzyl alcohol

Entry	Catalyst	Solvent	Time (h)	Selectivity (%)			Conversion (%)[b]
				Benzaldehyde	Benzoic acid	Benzyl benzoate	
1	**1a**	CH_2Cl_2	4	100	0	0	18
2	**1b**	CH_2Cl_2	4	98.5	0.2	0	23
3	**2**	CH_2Cl_2	4	100	0	0	17
4	**3**	CH_2Cl_2	4	100	0	0	17
5	**1a**	CH_2Cl_2	8	100	0	0	23
6	**1b**	CH_2Cl_2	8	95	5	0	28
7	**2**	CH_2Cl_2	8	100	0	0	25
8	**3**	CH_2Cl_2	8	100	0	0	28
9	**1a**	DMF	4	94	0	6	30
10	**1b**	DMF	4	60	0	40	49
11	**2**	DMF	4	78	0	22	38
12	**3**	DMF	4	89	0	11	54
13	**1a**	DMF	12	28	0	72	62
14	**1b**	DMF	12	41	0	59	58
15	**2**	DMF	12	20	0	80	64
16	**3**	DMF	12	49	0	51	58
17	-	DMF	12	100	0	0	11.7

[a] Reaction conditions: benzyl alcohol (1 mmol), TBHP (2.26 mmol), Solvent (1 ml), catalyst (0.063 mmol based on Cu), room temperature.

[b] GC yield is based on starting substrate.

Table 3[a] Catalytic activity of coordination polymers **1-3** in the oxidation of benzyl alcohol

Entry	Catalyst	Time (h)	Conversion (%)[b]	Selectivity (%)[c]
1	**1a**	4	65	86
2	**1a**	8	82	100
3	**1b**	4	67	90
4	**1b**	8	85	100
5	**2**	4	65	86
6	**2**	8	95	99
7	**3**	4	30	2
8	**3**	8	68	73
9	**3**	14	97	97
10	-	14	20	0

[a] Reaction conditions: benzyl alcohol (1 mmol), TBHP (2.26 mmol), catalyst (0.063 mmol based on Cu), CH_2Cl_2 (1 ml), 40 ºC.

[b] GC yield is based on starting substrate.

[c] Selectivity was determined towards the formation of benzoic acid.

To assess the catalytic effect of **1-3** catalysts on the oxidation process, the reaction was conducted without the catalysts under similar conditions both at room temperature and 40 ºC. The results show that benzyl alcohol undergoes insubstantial oxidation to benzaldehyde (with the conversion of 11.7 %) at room temperature using DMF solvent (Table 2, Entry 17). Performing the blank test at 40 ºC for 14 h in CH_2Cl_2 also led to low conversion of 20 % for oxidation of benzyl alcohol to benzaldehyde (Table 3, Entry 10).

Further studies of the catalytic parameters such as oxidant and catalyst amounts as well as substrate nature were carried out and the results are given in Table 4. By increasing the amount of oxidant from 2.26 mmol to 4.52 mmol, the reaction conversion in the presence of **1**-**3** reached 63-91 % after 8 h (Table 4, Entries 1-4). Also, the reaction conversion of 76-88 % was obtained after 6 h upon increasing of the catalyst amounts from 0.063 mmol to 0.126 mmol (Table 4, Entries 5-8). Comparing these results with the conversions reported in Table 3 shows that increasing the amounts of the catalysts led to the improvement of the reaction conversions.

In order to investigate the electronic effects of substrates on the oxidation reaction, 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol were tested as representative substrate models. After 4 h, the reaction conversion of 99 % was obtained using 4-methoxybenzyl alcohol (Table 4, Entries 9-12). More reactivity of this substrate compared to benzyl alcohol is due to the presence of methoxy group which supply more electrons. When 4-chlorobenzyl alcohol is used as the substrate, the oxidation reaction required more time (8 h) and the selectivity towards formation of the corresponding acid decreased (Table 4, Entries 13-16).

Table 4[a] Effects of oxidant and catalyst amounts as well as substrate nature on the oxidation reaction catalyzed by **1-3**

Entry	Substrate	Catalyst	Amount of catalyst (mmol)	Amount of TBHP (mmol)	Time (h)	Conversion (%)[b]	Selectivity (%)[c]
1	Benzyl alcohol	**1a**	0.063	4.52	8	88	94
2	Benzyl alcohol	**1b**	0.063	4.52	8	91	96
3	Benzyl alcohol	**2**	0.063	4.52	8	72	86
4	Benzyl alcohol	**3**	0.063	4.52	8	63	77
5	Benzyl alcohol	**1a**	0.126	2.26	6	83	88
6	Benzyl alcohol	**1b**	0.126	2.26	6	88	88
7	Benzyl alcohol	**2**	0.126	2.26	6	76	91
8	Benzyl alcohol	**3**	0.126	2.26	6	78	86
9	4-Methoxybenzyl alcohol	**1a**	0.063	2.26	4	100	100
10	4-Methoxybenzyl alcohol	**1b**	0.063	2.26	4	100	100
11	4-Methoxybenzyl alcohol	**2**	0.063	2.26	4	100	100
12	4-Methoxybenzyl alcohol	**3**	0.063	2.26	4	100	100
13	4-Chlorobenzyl alcohol	**1a**	0.063	2.26	8	100	37
14	4-Chlorobenzyl alcohol	**1b**	0.063	2.26	8	62	53
15	4-Chlorobenzyl alcohol	**2**	0.063	2.26	8	100	48
16	4-Chlorobenzyl alcohol	**3**	0.063	2.26	8	100	11

[a] Reaction conditions: Substrate (1 mmol), CH_2Cl_2 (1 ml), 40 ºC
[b] GC yield is based on starting substrate.
[c] Selectivity was determined towards the formation of acid.

The reusability of the obtained catalysts was examined in the oxidation of benzyl alcohol. After completion of the reaction, the catalysts were separated and washed with DMF. The reaction conditions were similar to those reported in Table 3 at 40 ºC using CH_2Cl_2 as solvent. The oxidation reactions were conducted for 14 h in the presence of reused **3** and for 8 h using recycled **1a**, **2** and **1b**. The results, given in Fig 9, displayed no appreciable loss in the activity and selectivity towards benzoic acid. Copper content of the catalysts before and after the reaction was determined by atomic absorption spectroscopy (Table 5). The results show negligible leaching of the catalysts. Moreover, the PXRD patterns of the fresh and recycled coordination polymers are similar (Fig. 2). These observations clearly confirm that the crystal structure of **1-3** catalysts remained intact upon the oxidation reactions, exhibiting the structural stability of the coordination polymers.

In the FT-IR spectra of **1-3** which are shown in Fig. 6, the characteristic peaks for the reused catalysts resemble those found in the spectra of their corresponding pristine coordination polymers. This observation points out that the structure of the catalysts has not been changed upon oxidation of benzyl alcohol.

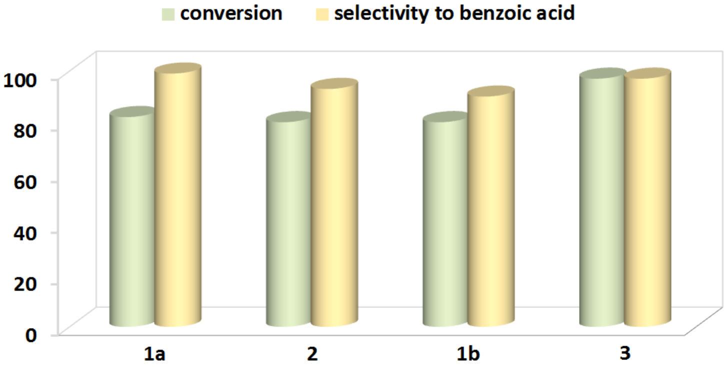


Fig. 9. Reusability of catalysts **1-3**

Table 5 Copper content of the catalysts which is determined by atomic absorption spectroscopy

Catalysts	Cu content in the catalysts (%)	
	Fresh	Reused
1a	23.27	22.25
2	18	16.24
1b	33.63	30.64
3	21.48	17.50

Based on the reported literature [45], benzyl alcohol oxidation over Cu^{2+} catalytic sites are attributed to a free radical pathway. The Cu^{2+} sites react with TBHP and form peroxo (t-BuOO$^{\cdot}$) and alkoxo (t-BuO$^{\cdot}$) radical species. The peroxo radicals react with benzyl alcohol and form the corresponding alcohol radical intermediate upon abstraction of benzylic hydrogen from the substrate. The intermediate reacts with t-BuO$^{\cdot}$ radical to generate t-BuOH and the oxidation products.

Benzyl alcohol oxidation was reported over MOF catalysts. Ling Peng *et al.* investigated the catalytic oxidation of benzyl alcohol to benzaldehyde over isostructural MOFs M(1,4-BDC)$(DABCO)_{0.5}$ [M = Co, Zn, Ni, Cu][30] with paddle wheel units. By employing Co(1,4-BDC)$(DABCO)_{0.5}$ as catalyst, 81.8 % conversion was obtained. Whereas in the presence of Cu(1,4-BDC)$(DABCO)_{0.5}$, a very low conversion (8.8 %) was achieved after 8 h. However, in our work, the Cu-based compounds with similar dinuclear units exhibited high conversions at lower temperature using less amounts of catalysts.

4. Conclusions

This study presents four new Cu(II)-based coordination polymers with similar SBUs. Compounds **1a** and **1b** are formed based on a mixture of μ_2-$MeCO_2$ and linear DABCO ligands. Coordination polymers **1a** and **1b** are polymorphous and comprise 1-D chains with similar connectivity and different packing structures. Compound **2** which is isostructural with the reported [Zn(1,4-BDC)$(DABCO)_{0.5}$], contains 1,4-BDC-Br and DABCO ligands. Compound **3** is a 2-D coordination polymer formed using 1,4-BDC-OH ligand. The resulting compounds were applied as heterogeneous catalysts for the oxidation of benzyl alcohol. They displayed selectivity to the formation of benzoic acid at 40 ºC in CH_2Cl_2 solvent and could be recycled and reused with maintenance of catalytic performance.

Acknowledgements

We gratefully acknowledge University of Tehran and Iran National Science Foundation: INSF [post-doctoral grant no. 95002447] for the financial support.

References

[1] R. Ciriminna, V. Pandarus, F. Béland, Y.-J. Xu, M. Pagliaro, Heterogeneously catalyzed alcohol oxidation for the fine chemical industry, Org. Process Res. Dev. 19 (2015) 1554-1558.

[2] C.P. Vinod, K. Wilson, A.F. Lee, Recent advances in the heterogeneously catalysed aerobic selective oxidation of alcohols, J. Chem. Technol. Biotechnol. 86 (2011) 161-171.

[3] D. Li, Q. Xu, Y. Li, Y. Qiu, P. Ma, J. Niu, J. Wang, A Stable Polyoxometalate-based metal–organic framework as highly efficient heterogeneous catalyst for oxidation of alcohols, Inorg. Chem. 58 (2019) 4945-4953.

[4] B. Kaboudin, H. Khanmohammadi, F. Kazemi, Polymer supported gold nanoparticles: Synthesis and characterization of functionalized polystyrene-supported gold nanoparticles and their application in catalytic oxidation of alcohols in water, Appl. Surf. Sci. 425 (2017) 400-406.

[5] J. Xu, J.-K. Shang, Y. Chen, Y. Wang, Y.-X. Li, Palladium nanoparticles supported on mesoporous carbon nitride for efficiently selective oxidation of benzyl alcohol with molecular oxygen, Appl. Catal., A 542 (2017) 380-388.

[6] P. Das, N. Aggarwal, N.R. Guha, Solid supported Ru(0) nanoparticles: an efficient ligand-free heterogeneous catalyst for aerobic oxidation of benzylic and allylic alcohol to carbonyl, Tetrahedron Lett. 54 (2013) 2924-2928.

[7] Y. Hong, X. Jing, J. Huang, D. Sun, T. Odoom-Wubah, F. Yang, M. Du, Q. Li, Biosynthesized bimetallic Au–Pd nanoparticles supported on TiO_2 for solvent-free oxidation of benzyl alcohol, ACS Sustainable Chem. Eng. 2 (2014) 1752-1759.

[8] Y. Li, Y. Hu, X.-F. Wu, Non-noble metal-catalysed carbonylative transformations, Chem. Soc. Rev. 47 (2018) 172-194.

[9] M. Aghajani, E. Safaei, B. Karimi, Selective and green oxidation of sulfides in water using a new iron(III) bis(phenol) amine complex supported on functionalized graphene oxide, Synth. Met. 233 (2017) 63-73.

[10] K.C. Gupta, A. Kumar Sutar, C.-C. Lin, Polymer-supported Schiff base complexes in oxidation reactions, Coord. Chem. Rev. 253 (2009) 1926-1946.

[11] A.R. Judy Azar, E. Safaei, S. Mohebbi, A novel Schiff base of Mn(III) complex supported on magnetic cobalt nanoparticles as a highly efficient retrievable heterogeneous catalyst in oxidation of alcohols and sulfides compounds, Mater. Res. Bull. 70 (2015) 753-761.

[12] R. Antony, R. Marimuthu, P. Vishnoi, R. Murugavel, Ethoxysilane appended M(II) complexes and their SiO_2/MCM-41 supported forms as catalysts for efficient oxidation of secondary alcohols, Inorg. Chim. Acta 469 (2018) 173-182.

[13] K.O. Xavier, J. Chacko, K.K. Mohammed Yusuff, Zeolite-encapsulated Co(II), Ni(II) and Cu(II) complexes as catalysts for partial oxidation of benzyl alcohol and ethylbenzene, Appl. Catal., A 258 (2004) 251-259.

[14] V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram, H.S. Rama, Catalytic oxidation by polymer-supported copper(II)–l-valine complexes, J. Mol. Catal. A: Chem. 208 (2004) 21-32.

[15] V.K. Bansal, P.P. Thankachan, R. Prasad, Oxidation of benzyl alcohol and styrene using H_2O_2 catalyzed by tetraazamacrocycle complexes of Cu(II) and Ni(II) encapsulated in zeolite-Y, Appl. Catal., A 381 (2010) 8-17.

[16] P. Cruz, Y. Pérez, I. del Hierro, M. Fajardo, Copper, copper oxide nanoparticles and copper complexes supported on mesoporous SBA-15 as catalysts in the selective oxidation of benzyl alcohol in aqueous phase, Microporous Mesoporous Mater. 220 (2016) 136-147.

[17] C.-C. Du, X.-F. Wang, S.-B. Zhou, D.-Z. Wang, D. Jia, New complexes constructed from in situ nitration of (1H-tetrazol-5-yl)phenol: synthesis, structures and properties, CrystEngComm 19 (2017) 6758-6777.

[18] S.-B. Zhou, X.-F. Wang, C.-C. Du, D.-Z. Wang, D. Jia, A series of new mixed-ligand complexes based on 3,6-bis(imidazol-1-yl)pyridazine: syntheses, structures, and catalytic activities, CrystEngComm 19 (2017) 3124-3137.

[19] Q. Yang, Q. Xu, H.-L. Jiang, Metal-organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis, Chem. Soc. Rev. 46 (2017) 4774-4808.

[20] S.M.J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A.I. Olivos-Suarez, A. Sepulveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E.V. Ramos-Fernandez, F.X. Llabres i Xamena, V. Van Speybroeck, J. Gascon, Metal-organic and covalent organic frameworks as single-site catalysts, Chem. Soc. Rev. 46 (2017) 3134-3184.

[21] L. Asgharnejad, A. Abbasi, M. Najafi, J. Janczak, Synthesis and structure of three new alkaline earth metal–organic frameworks with high thermal stability as catalysts for Knoevenagel condensation, Cryst. Growth Des. 10.1021/acs.cgd.8b01810.

[22] H. Han, S. Zhang, H. Hou, Y. Fan, Y. Zhu, Fe(Cu)-Containing coordination polymers: syntheses, crystal structures, and applications as benzyl alcohol oxidation catalysts, Eur. J. Inorg. Chem. 2006 (2006) 1594-1600.

[23] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Aerobic oxidation of benzylic alcohols catalyzed by metal−organic frameworks assisted by TEMPO, ACS Catal. 1 (2011) 48-53.

[24] S. Aryanejad, G. Bagherzade, A. Farrokhi, A nanoscale Cu-metal organic framework with Schiff base ligand: synthesis, characterization and investigation catalytic activity in the oxidation of alcohols, Inorg. Chem. Commun. 81 (2017) 37-42.

[25] J. Hou, Y. Luan, J. Tang, A.M. Wensley, M. Yang, Y. Lu, Synthesis of UiO-66-NH_2 derived heterogeneous copper (II) catalyst and study of its application in the selective aerobic oxidation of alcohols, J. Mol. Catal. A: Chem. 407 (2015) 53-59.

[26] Y. Qi, Y. Luan, J. Yu, X. Peng, G. Wang, Nanoscaled copper metal–organic framework (MOF) based on carboxylate ligands as an efficient heterogeneous catalyst for aerobic epoxidation of olefins and oxidation of benzylic and allylic alcohols, Chem. – Eur. J. 21 (2015) 1589-1597.

[27] M. Najafi, A. Abbasi, M. Masteri-Farahani, V.H.N. Rodrigues, Synthesis, characterization and crystal structure of a copper molybdate coordination polymer as an epoxidation catalyst, Inorg. Chim. Acta 433 (2015) 21-25.

[28] S. Abednatanzi, A. Abbasi, M. Masteri-Farahani, Post-synthetic modification of nanoporous $Cu_3(BTC)_2$ metal-organic framework via immobilization of a molybdenum complex for selective epoxidation, J. Mol. Catal. A: Chem. 399 (2015) 10-17.

[29] G. Kumar, F. Hussain, R. Gupta, Copper based coordination polymers based on metalloligands: utilization as heterogeneous oxidation catalysts, Dalton Trans. 47 (2018) 16985-16994.

[30] L. Peng, S. Wu, X. Yang, J. Hu, X. Fu, Q. Huo, J. Guan, Application of metal organic frameworks M(bdc)(ted)$_{0.5}$ (M = Co, Zn, Ni, Cu) in the oxidation of benzyl alcohol, RSC Adv. 6 (2016) 72433-72438.

[31] Y. Zhao, H. Wu, T.J. Emge, Q. Gong, N. Nijem, Y.J. Chabal, L. Kong, D.C. Langreth, H. Liu, H. Zeng, J. Li, Enhancing gas adsorption and separation capacity through ligand functionalization of microporous metal–organic framework structures, Chem. – Eur. J. 17 (2011) 5101-5109.

[32] Y. Gao, J.M. Klunder, R.M. Hanson, H. Masamune, S.Y. Ko, K.B. Sharpless, Catalytic asymmetric epoxidation and kinetic resolution: modified procedures including in situ derivatization, J. Am. Chem. Soc. 109 (1987) 5765-5780.

[33] G. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr., Sect. C 71 (2015) 3-8.

[34] D.N. Dybtsev, H. Chun, K. Kim, Rigid and Flexible: A Highly porous metal–organic framework with unusual guest-dependent dynamic behavior, Angew. Chem. Int. Ed. 43 (2004) 5033-5036.

[35] H. Wang, J. Getzschmann, I. Senkovska, S. Kaskel, Structural transformation and high pressure methane adsorption of Co_2(1,4-bdc)$_2$dabco, Microporous Mesoporous Mater. 116 (2008) 653-657.

[36] Z. Liang, M. Marshall, A.L. Chaffee, CO_2 adsorption, selectivity and water tolerance of pillared-layer metal-organic frameworks, Microporous Mesoporous Mater. 132 (2010) 305-310.

[37] M.A. Alavi, A. Morsali, Synthesis and characterization of different nanostructured copper(II) metal-organic frameworks by a ligand functionalization and modulation method, CrystEngComm 16 (2014) 2246-2250.

[38] Z. Chen, S. Xiang, H.D. Arman, P. Li, S. Tidrow, D. Zhao, B. Chen, A microporous metal–organic framework with immobilized –OH functional groups within the pore surfaces for selective gas sorption, Eur. J. Inorg. Chem. 2010 (2010) 3745-3749.

[39] A.Q. Wang, T.D. Golden, Electrodeposition of oriented cerium oxide films, Int. J. Electrochem. 2013 (2013) 10.

[40] K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser, Y.J. Chabal, Stability and hydrolyzation of metal-organic frameworks with paddle-wheel SBUs upon hydration, Chem. Mater. 24 (2012) 3153-3167.

[41] L. Asgharnejad, A. Abbasi, A. Shakeri, Ni-based metal-organic framework/GO nanocomposites as selective adsorbent for CO_2 over N_2, Microporous Mesoporous Mater. 262 (2018) 227-234.

[42] J.Y. Lee, D.H. Olson, L. Pan, T.J. Emge, J. Li, Microporous metal–organic frameworks with high gas sorption and separation capacity, Adv. Funct. Mater. 17 (2007) 1255-1262.

[43] R. Bikas, F. Ajormal, M. Emami, N. Noshiranzadeh, A. Kozakiewicz, Catalytic oxidation of benzyl alcohols by new Cu(II) complexes of 1,3-oxazolidine based ligand obtained from a solvent free reaction, Inorg. Chim. Acta 478 (2018) 77-87.

[44] G.C. Behera, K.M. Parida, Liquid phase catalytic oxidation of benzyl alcohol to benzaldehyde over vanadium phosphate catalyst, Appl. Catal., A 413-414 (2012) 245-253.

[45] N. Gogoi, T. Begum, S. Dutta, U. Bora, P.K. Gogoi, Rice husk derived nanosilica supported Cu(II) complex: an efficient heterogeneous catalyst for oxidation of alcohols using TBHP, RSC Adv. 5 (2015) 95344-95352.

Highlights:

- New coordination polymers with paddle-wheel SBUs were solvothermally synthesized.
- They were applied as heterogeneous catalysts for the oxidation of benzyl alcohol.
- The catalysts displayed good activity and stability in the oxidation reaction.