

Bimetallic MOFs as Catalysts for Efficient and Totally Selective Oxidation of Benzylic Alcohols at Ambient Conditions

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The catalytic activity of bimetallic MOFs known as STA-12 (M_1, M_2) ($M_{1,2} = \text{Mn, Fe, Co}$) was investigated in the oxidation of benzylic alcohols to corresponding aldehydes at ambient conditions. The oxidation reaction with $\text{Na}_2\text{S}_2\text{O}_4/\text{TBHP}$ (tert-butyl hydroperoxide) mixture shows total selectivity and excellent efficiency under desired reaction times. The heterogeneous catalyst displays high reusability and stability for the ten consecutive reactions without decreasing in yield and selectivity. To identify radical species responsible for the oxidation process, selective scavenging experiments were performed and a proposed oxidation mechanism was discussed.

Keywords: Heterogeneous catalysis, Bimetallic MOFs, Alcohol oxidation, STA-12

INTRODUCTION

Selective and efficient oxidation of alcohols to aldehydes is an essential reaction in organic chemistry and an important part of laboratory research and industrial production of many drugs and materials. Many continuous efforts are made to develop efficient technologies for alcohol oxidation [1]. Typically, the liquid phase oxidation of alcohols is carried out with inorganic oxidant, which suffers from many disadvantages, such as the consumption of expensive materials and the production of toxic waste. In the past few decades, catalytic processes have been developed for green and economical oxidation of alcohols using oxidizing materials such as molecular oxygen, hydrogen peroxide and organic peroxide [2,3]. On the other hand, these methods use homogeneous catalysts based on molecular complexes of transition metals such as cobalt, copper, iron, and manganese, which are difficult to recover from the reaction mixture. Therefore, research is necessary to prepare new and efficient heterogeneous catalysts [4].

Metal-organic frameworks (MOFs) are the emerging porous solids materials consisting of metal ions or metal

clusters that occupy nodal positions in a crystalline framework. These nodes are connected through organic ligands to produce maximum surface area with adjustable porosity [5]. These materials have provided an excellent opportunity to design a new generation of efficient catalysts in the liquid phase. The high porosity and open framework structure of MOFs permit the availability of many active single catalytic sites and accelerate the transport of reactants. Also, due to their heterogeneity and easy recoverability have the advantage of heterogeneous catalysts [6]. However, a review of the scientific literature shows that the catalytic properties of MOFs are limited to MOFs made of carboxylic acid and imidazolate ligands, and those containing phosphonic acid ligands have been rarely used [7-9]. Therefore, the insight into their catalytic properties on significant reactions such as selective oxidation of alcohols could be an interesting study.

Encouraged by promising results on the catalytic performance of phosphonate-based MOFs in alcohol oxidation, we wish to extend our research toward catalytic oxidation of alcohols using phosphonate-based bimetallic STA-12 MOFs containing Mn, Fe and Co atoms. Due to the probable synergistic effects that derive from the existence of two or more metals, mixed-metal MOFs can display higher

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efficiency compared to single-metal MOFs [10]. In this research, the efficiency of the bimetallic STA-12 family of MOFs has been investigated in a new heterogeneous catalytic system for the selective oxidation of alcohols to related aldehydes. A mixture of TBHP and Na₂S₂O₄ (sodium dithionite) was applied as the leading agent for alcohol oxidation. As far as we have examined, this is the first report that mixed-metal phosphonate-based MOFs are used to selective synthesis of aromatic aldehydes and ketones from alcohols without the formation of carboxylic acids, in a short time and under ambient conditions.

EXPERIMENTAL

Chemicals and Reagents

Cobalt nitrate hexahydrate, iron chloride tetrahydrate, manganese acetate tetrahydrate, nickel nitrate tetrahydrate, ethyl acetate, tert-butyl hydroperoxide (70% w/w), hydrochloric acid, nitrobenzene and phenol were purchased from Merck. Piperazine, formaldehyde, sodium dithionite (Na₂S₂O₄), sodium sulfate, sodium thiosulfate and sodium persulfate (Na₂S₂O₈) were purchased from Sigma-Aldrich. All of the chemicals were purchased with the purity of analytical grade and used without more purification.

Synthesis of Bisphosphonate Ligand (H₄L)

Organic linker, 1,4-bis (phosphonomethyl) piperazine, [H₂O₃P-CH₂-NC₄H₈N-CH₂-PO₃H₂], were synthesized according to the previously reported method [8] and characterized with IR, ³¹P NMR, ¹H NMR, ¹³C NMR spectroscopy and elemental analysis (Supporting Informations, Figs. S1-S4).

Synthesis of MOFs

Bimetallic MOFs with the structure of STA-12 (M₁, M₂) containing cobalt, iron, and manganese ions are synthesized according to the reported method [11,12].

Instrumentation

Progression of the reaction was followed by TLC using SIL G/UV 254 silica gel sheets and GC on a Shimadzu GC-16A apparatus with a CBP1-25 capillary column. The IR spectra were obtained with the Nicolet 800 spectrometer. NMR spectra were obtained with Bruker Avance DPX

devices at 400 MHz. For elemental analysis, CHN analysis (Heraeus CHN-O-RAPID) and ICP-AES method (Perkin-Elmer Optima 7300DV) were used. X'PERT PRO diffractometer with Cu-K_α radiation was applied to record the powder X-ray diffraction patterns. The Avaspec-2048-TEC spectrometer was used to record the UV-Vis spectra. The surface properties of the catalysts were investigated with the Belsorp Mini II. The solids were placed in a vacuum for 5 h at 100 °C and ads/des isotherms of N₂ were recorded at 77 K. The thermal stability of the MOFs were investigated with TGA (NETZSCH TG 209 F1 Iris) method with a heating rate of 10 °C.min⁻¹ from 25 to 900 °C.

Alcohols Oxidation Experiment

27.4 μL TBHP (70%) (0.5 mmol) and 0.2 mmol Na₂S₂O₄ were poured in a mixture of 1 mL of ethyl acetate, 0.1 mmol of alcohol, and 2 mg of catalyst. The reaction was stirred for a specified time at ambient temperature and the reaction progression was assessed by measuring the amount of aldehyde produced by TLC or GC. The exact amount of reaction products was measured by GC. At the end of the process, the catalyst was easily removed by adding ethyl acetate to the reaction vessel and centrifugation.

Catalyst Recovering

The reusability of the MOFs in the reaction of 4-chlorobenzyl alcohol was investigated. At the end of the reaction, 2 mL ethyl acetate was added to the reaction vessel and MOF was separated by centrifugation. The isolated catalyst was washed with 1 mL ethyl acetate and dried at 60 °C and used in a consequent reaction with a fresh substrate.

RESULT AND DISCUSSION

Initial Evaluation of Reaction Conditions and Efficiency of Catalysts

At first, the performance of the synthesized MOFs in the oxidation reaction of 4-chlorobenzyl alcohol at room temperature for 2 h has investigated (for more informations on the catalyst identification and data analysis, see Supporting Informations and reference [11]. In the initial evaluating reactions, the oxidizing mixture of TBHP/Na₂S₂O₄ in the presence of 2 mg of catalyst in ethyl

Table 1. Evaluation of Different Situations for the Oxidation Process of 4-Chlorobenzyl Alcohol with Synthesized Catalysts^a

Entry	Catalyst	Oxidant mixture	Conversion (%) ^b
1	STA-12 (Mn, Co)	TBHP/Na ₂ S ₂ O ₄	85
2	STA-12 (Co, Fe)	TBHP/Na ₂ S ₂ O ₄	60
3	STA-12 (Mn, Fe)	TBHP/Na ₂ S ₂ O ₄	65
4	H ₄ L	TBHP/Na ₂ S ₂ O ₄	25
5	Mn(OAc) ₂ , 4H ₂ O	TBHP/Na ₂ S ₂ O ₄	20
6	Co(NO ₃) ₂ , 6H ₂ O	TBHP/Na ₂ S ₂ O ₄	25
7	FeCl ₂ , 4H ₂ O	TBHP/Na ₂ S ₂ O ₄	15
8	-	TBHP/Na ₂ S ₂ O ₄	12
9	STA-12 (Mn, Co)	Na ₂ S ₂ O ₄ /H ₂ O ₂	25
10	STA-12 (Mn, Co)	Na ₂ S ₂ O ₄ /Oxone	10
11	STA-12 (Mn, Co)	Na ₂ S ₂ O ₄ /UHP	18
12	STA-12 (Mn, Co)	Na ₂ S ₂ O ₄ /Air	n.r
13	STA-12 (Mn, Co)	TBHP ^c /Na ₂ S ₂ O ₄	83
14	STA-12 (Mn, Co)	Na ₂ S ₂ O ₄	n.r
15	STA-12 (Mn, Co)	TBHP	Trace
16	STA-12 (Mn, Co)	TBHP/Na ₂ S ₂ O ₃	n.r
17	STA-12 (Mn, Co)	TBHP/Na ₂ SO ₄	n.r
18	STA-12 (Mn, Co)	TBHP/Na ₂ S ₂ O ₈	Trace

Reaction conditions: ^aAlcohol (0.1 mmol), solvent (ethyl acetate, 0.5 mL), catalyst (2 mg), ratio of alcohol:Na₂S₂O₄:oxidant (1:2:4), time (2 h) at ambient temperature. ^bWas measured by GC and chlorobenzene as standard. ^cProcess with dry TBHP. In all reactions, selectivity was 100%. nr: No reaction

acetate was used (Table 1, rows 1-3). Fortunately, the oxidation system of MOF/Na₂S₂O₄/TBHP showed good to excellent catalytic activity. Besides, STA-12 (Mn, Co) showed better performance than other synthesized MOFs (Table 1, row 3). As shown in Table S2, STA-12 (Mn, Co), compared to the other catalysts, have the higher surface

area, average pore diameter and total pore volume. Therefore has a more efficient adsorption capability for reactants in its framework. This sample has a lower intensity and broader peaks in its PXRD pattern (Fig. S7), which may be related to its lower crystallinity and existence of structural defects in the framework structure, providing

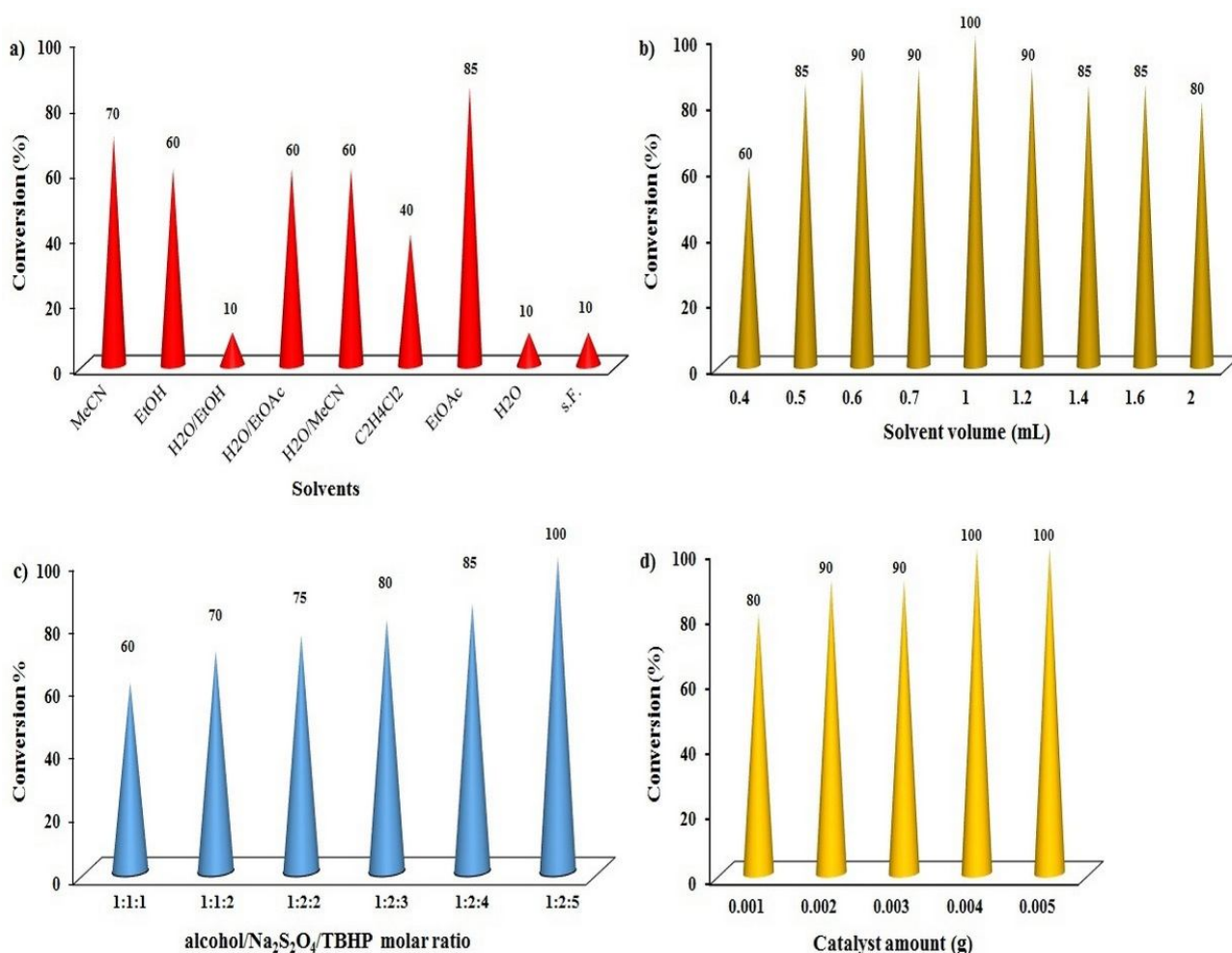


Fig. 1. The optimizations of the (a) solvent nature (b) solvent volume (c) molar ratio of alcohol/ Na₂S₂O₄/TBHP and (d) catalyst amount for 4-chlorobenzyl alcohol oxidation accelerated by STA-12 (Mn, Co). Other conditions: alcohol (0.1 mmol), solvent (EtOAc, 0.5 mL), catalyst (2 mg), alcohol:Na₂S₂O₄:oxidant proportion: 1:2:4, ambient temperature, time (2 h).

unsaturated coordination sites and improve the catalytic property [13,14]. On the other hand, a comparison of the results shows that STA-12 (Mn, Co) had a higher efficiency in selective oxidation of benzyl alcohols with respect to STA-12 (Mn) and STA-12 (Co) [9]. This can be attributed to the above mentioned properties of STA-12 (Mn, Co) and synergy of Mn and Co atoms in the structure.

It is noteworthy that the replacement of the MOF catalyst with the free bisphosphonate ligand and the metal salts significantly reduces the oxidation efficiency (Table 1, rows 4 to 7). These results show that the adsorption of

reactants in the pores of the metal-organic framework is of great importance in promoting the reaction [15].

Due to these promising results, other reaction conditions were assessed for the oxidation of 4-chlorobenzyl alcohol as a model reactant with the STA-12 (Mn, Co)/Na₂S₂O₄/TBHP oxidizing system (Table 1 and Fig. 1).

Investigation of the effect of nature and the amount of solvent on the progression of the oxidation reaction showed that 1 mL of EtOAc as a green solvent is preferable for this oxidation method (Figs. 1a and b). Experiments were accomplished to evaluate the effect of other oxidants on the

reaction efficiency (Table 1, rows 9 to 12), but the oxidation process was significantly diminished. The results revealed that the 1:2:5 molar ratio of TBHP/ $\text{Na}_2\text{S}_2\text{O}_4$ /alcohol is more convenient for the catalytic procedure and increasing the amount of TBHP does not increase the reaction yield (Fig. 1c). Additional studies corroborate that the existence of $\text{Na}_2\text{S}_2\text{O}_4$ and TBHP is vital for efficient oxidation of alcohol (Tables 1, rows 14 and 15) and the reaction yield did not change in the presence of dry TBHP (Table 1, rows 13). It was found that reducing the catalyst amount by up to 6 mol% reduces the oxidation yield while increasing the catalyst value by 10.3 mol% does not improve the reaction efficiency (Fig. 1d).

Heterogeneity and Reusability Test

To verify the heterogeneity of the method, the oxidation reaction of 4-chlorobenzyl alcohol has stopped after reaching 40% progress, the catalyst was removed from the process, and the reaction was continued under optimized conditions (Fig. S10). In the absence of the catalyst, the oxidation of alcohol finally reached 70% after 12 h, consistent with the result obtained in conditions without catalyst [16]. Also, the results of elemental analysis for the reaction mixture by the ICP-AES technique did not show cobalt and manganese ions after separation of the catalyst. Therefore, it can be concluded that the continuation of the alcohol oxidation reaction without the catalyst was carried out under the influence of the TBHP/ $\text{Na}_2\text{S}_2\text{O}_4$ oxidant mixture. Also, selectivity for aldehyde production was 100% during the reaction time and no other by-product was observed (Fig. S10). To evaluate the reusability of STA-12 (Mn, Co), the isolated catalyst from the reaction vessel after washing with ethyl acetate and drying at 60 °C was reused in the oxidation reaction. This test was repeated 10 times, but no reduction in reaction yield was observed, demonstrating the high reusability and robustness of metal-organic frameworks based on phosphonate ligands (Fig. S11). Further confirmation of this claim was obtained by examining the structure of the recovered catalyst through PXRD and infrared spectroscopy. The results do not differ from the data obtained from the fresh catalyst (Fig. S12) and indicate the excellent structural stability of STA-12 (Mn, Co).

Catalytic Oxidation of Different Types of Alcohols

The performance of the oxidation system under optimized conditions was studied for the oxidation of various alcohols (Table 2). Aldehydes and ketones were produced from the corresponding benzylic alcohols with electron donor substitutes by excellent yield and 100% selectivity during an adequate reaction time (Table 2, rows 1, 2, 3 and 5-7). However, for benzylic alcohols with electron-withdrawing substitutes, the efficiency decreased significantly (Table 2, rows 4, 8 and 14). The decrease in product yield in α -hydroxy ketone (row 8) is also due to the electron-withdrawing effect of the carbonyl group at the α position. To answer whether the reactants react after entering the catalyst pores, two alcohols larger than benzyl alcohol were examined (rows 9 and 10). The results show that as the molecule size increases, the reaction rate decreases significantly. This phenomenon shows that the MOF with the catalytically active sites in its pores accelerates the reaction process. It is noteworthy that heterocyclic aromatic alcohols such as pyridine 2-yl methanol and furfuryl alcohol do not react in this catalytic system (Table 2, rows 11 and 12). Also, oxidation of aliphatic alcohol, like cyclohexyl alcohol, does not progress well (Table 2, row 13). The competitive oxidation between the alkene and alcohol functional groups resulted in the selective alcohol oxidation, which indicates the chemical selectivity of this protocol to the oxidation of alcohols (Table 2, row 14). The oxidation reaction of 20 mmol of alcohol was very efficient and it reveals that the oxidation protocol is effective on a larger scale (Table 2, row 3).

Identification of Effective Oxidative Species

Several experiments were accomplished to identify species that are responsible for the oxidation reaction. No change in oxidation efficiency was observed in the Ar inert atmosphere (Table 2, row 3), indicating TBHP as the principal oxidizing agent. On the other hand, after adding radical scavengers such as BHT (butylated hydroxytoluene) and TEMPO to the reaction vessel, a significant reduction in reaction yields was observed, demonstrating the oxidation process is controlled by reactive radicals (Fig. 2). Activation of the oxidizing mixture $\text{Na}_2\text{S}_2\text{O}_4$ /TBHP with MOF can produce the sulfate radical anion ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals ($\cdot\text{OH}$) [17]. To detect the predominant species in

Table 2. Alcohols Oxidation under STA-12 (Mn, Co)/TBHP/Na₂S₂O₄ Catalytic System^a

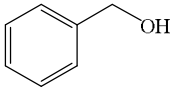
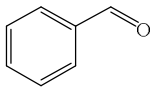
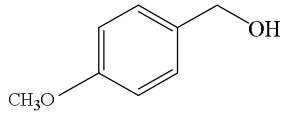
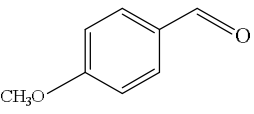
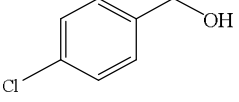
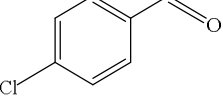
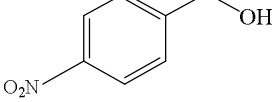
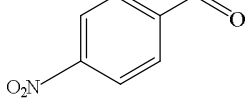
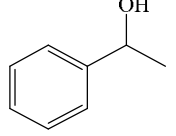
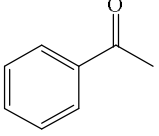
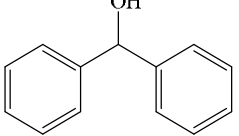
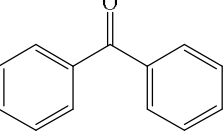
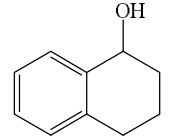
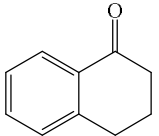
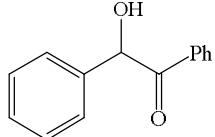
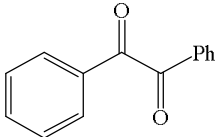
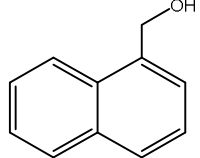
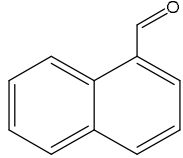
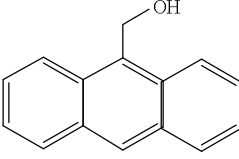
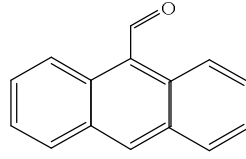
Entry	Substrate	Product	Conversion (%) ^b	TOF ^c
1			93 (80) ^d	9.72
2			100 (80)	9.72
3			95 (80) (98) ^e (98) ^f	9.72
4			37 (30)	3.65
5			100 (80)	9.72
6			80 (40)	4.86
7			80 (60)	7.29
8			25 (20)	2.43
9			48 (30)	3.65
10			25 (10)	1.21

Table 2. Continued

11			Trace	-
12			Trace	-
13			10 (5)	0.6
14			30 (10)	1.21

^aReaction conditions: Alcohol (0.1 mmol), solvent (ethyl acetate, 1 mL), ratio of alcohol:Na₂S₂O₄:oxidant (1:2:5), catalyst (4 mg), time (2 h) at room temperature. ^bWas measured with GC and chlorobenzene as an internal standard. ^cCalculated based on the formula [catalyst mmol/product mmol per hour]. ^dProduct yield after 1 h. ^eYield with 20 mmol of alcohol. ^fThe reaction was performed in the Ar inert atmosphere.

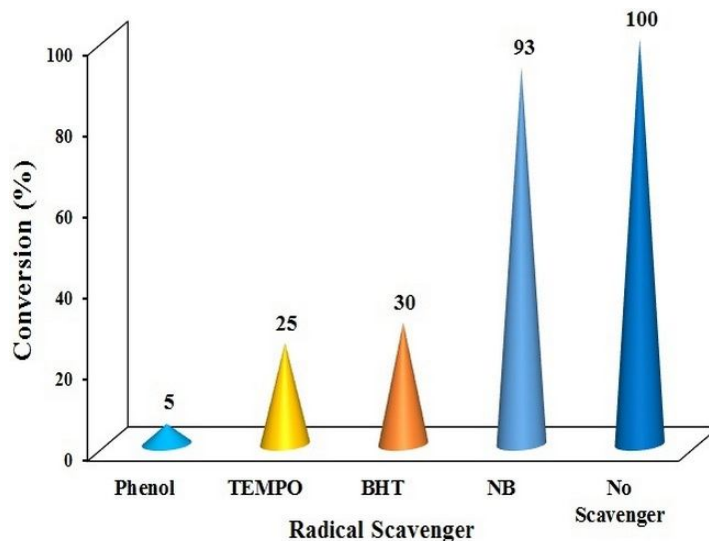


Fig. 2. Radical trapping tests for the reaction of 4-chlorobenzyl alcohol with STA-12 (Mn, Co)/TBHP/Na₂S₂O₄ catalytic system (scavenger value: 650 mM).

the oxidation system, a selective radical trapping experiment was performed using nitrobenzene (NB) and phenol. NB responds mainly to hydroxyl radicals, but phenol is a reported trapping agent for both SO₄^{•-} and [•]OH

radicals [18]. Adding phenol to the oxidation reaction significantly reduced the reaction yield to 5%. However, in the presence of NB, a slight decrease in oxidation efficiency occurred.

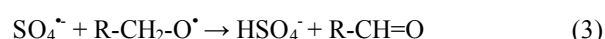
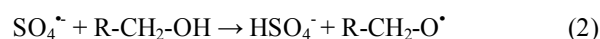
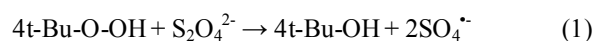
Table 3. Comparison of the Present Catalytic System with other MOFs in the Oxidation of 4-Methoxy Benzyl Alcohol

Entry	Catalytic system	Reaction conditions	Time (h)	Catalyst mass	Selectivity (%)	Conversion (%)	Ref.
1	Pd/COF-300	O ₂ /Toluene/90 °C	48	10 mg	>99	97	[21]
2	UiO-67-bpy-Eu	Air/TEMPO/toluene-AcOH/60 °C	18	2 mg	>99	99	[22]
3	CuNi/MIL-101	O ₂ /THF/100 °C	4	40 mg	23.8	87.9	[23]
4	MOF-808-V-Hf	O ₂ /Toluene/105 °C	8	66 mg	>99	75	[24]
5	MIL-101-Au-Ni	O ₂ /THF/80 °C	4	20 mg	99.1	45	[25]
6	NU-1200-Zr-V	O ₂ /Toluene/1,2-dichlorobenzene/105 °C	11	47 mg	>99	100	[26]
7	STA-12 (Co)	TBHP/EtOAc/60 °C	1.5	2 mg	>99	65	[8]
8	STA-12 (Mn)	TBHP/Na ₂ S ₂ O ₄ /EtOAc/25 °C	2	2 mg	>99	70	[9]
9	STA-12 (Co)	TBHP/Na ₂ S ₂ O ₄ /EtOAc/25 °C	2	2 mg	>99	70	[9]
10	STA-12 (Mn, Co)	TBHP/Na ₂ S ₂ O ₄ /EtOAc/25 °C	2	4 mg	>99	100	This work

These observations indicate the sulfate radical as the predominant oxidant agent advancing the oxidation process. The SO₄^{•-} radical is more suitable than the hydroxyl radical for the oxidation of many organic compounds because it promotes oxidation more selectively through electron transfer and hydrogen abstraction. Also, It has more stability and a longer lifetime compared to [•]OH radicals [19].

In the experiments that sodium dithionate (Na₂S₂O₄) was replaced with sodium sulfate (Na₂SO₄) and sodium thiosulfate (Na₂S₂O₃), no oxidation reaction was occurred (Tables 1, rows 16 and 17). However, the related aldehyde was not attained using Na₂S₂O₈/TBHP combination as an oxidant (Table 1, row 18) and excessive oxidation to the carboxylic acid was detected. These observations reveal that the SO₄^{•-} radical is not created from the above combinations. The proposed mechanism for the oxidation reaction of alcohols by the Na₂S₂O₄/TBHP mixture in the presence of the STA-12 (Mn, Co) catalyst can be presented as follows (Eqs. (1)-(3)). Initially, the sulfate radical is produced by the reaction of TBHP and S₂O₄²⁻ anion. Alcohol reacts with the

sulfate radical in two steps to give the related aldehyde [20].



To demonstrate the competency of the presented method, the data obtained for the reaction of 4-methoxy benzyl alcohol compared with the recently published results for other metal-organic frameworks [21-26] (Table 3). A review of the information shows the superiority of the proposed oxidation method in terms of high production efficiency, excellent selectivity, short reaction time, a small amount of catalyst, and ambient conditions.

CONCLUSIONS

In this research, three bimetallic MOFs based on bisphosphonate ligand with the structure of STA-12 have

been used for selective heterogeneous catalytic oxidation of the benzylic alcohols to the related aldehyde. Alcohol oxidation was accomplished in a short time, under ambient conditions, and with high efficiencies. The catalyst has significant stability and high reusability in the consecutive reactions without efficiency and selectivity loss. Also, using a cheap and available oxidizing mixture ($\text{Na}_2\text{S}_2\text{O}_4/\text{TBHP}$) with a small amount of catalyst in ethyl acetate as a green solvent makes the method presented in this research convenient for practical purposes.

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