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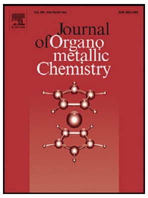

Fabrication of a new heterogeneous tungstate-based on the amino-functionalized metal-organic framework as an efficient catalyst towards sonochemical oxidation of alcohols under green condition

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ABSTRACT

Ultrasonic-assisted reactions, as a green technique, are often more efficient compared to those traditional protocols. To this end, the selective and solvent-free oxidation of aromatic alcohols to the corresponding aldehydes and ketones were investigated in the presence of Co-ABDC/W at room temperature under ultrasonic irradiation conditions for the first time in this paper. The structure, particle size, thermal stability, and morphology of the fabricated heterogeneous catalyst and the products were characterized by FT-IR, EDS, FE-SEM, XRD, TGA, and GC analyses. In this regard, immobilization of tungstate had a significant effect on thermal stability (around 450 °C for 40% weight loss) and catalytic performance. Moreover, the efficiency of two different oxidation methods, including ultrasound irradiations and reflux, were comparatively investigated by GC spectrometry. Obtained sonoxidation results presented higher conversions ranging (84 to 100%) than reflux condition via shorter reaction times. The influences of the reaction parameters, such as hydrogen peroxide concentration, and catalyst loading, were also investigated. The proposed method offers several advantages, such as excellent conversions, selective oxidations, environmentally-benign procedure, short reaction times, and easy workup. Notably, this is the first report that focuses on using amino-functionalized MOFs with ultrasonic irradiation for selective oxidation reactions.

1. Introduction

The oxidation of alcohols to carbonyl compounds is known as a pivotal functional group transformation which is basically important for the environment, life, and synthetic chemistry [1]. Traditional alcohol oxidation methods involve transition metals, such as stoichiometric oxidants, that are not only toxic but also release considerable amounts of side products [2]. Therefore, developing an alternative methodology using a clean energy source and green oxidants is really essential. Ultrasonic irradiation has attracted considerable attention by researchers for its diverse applications. In comparison with traditional protocols, ultrasonic accelerated reactions are faster, more convenient, simple, and easily controlled. In addition to accelerating organic reactions, it is also possible to decrease the number of required stages for these types of techniques. The acceleration of ultrasonic-assisted reactions can be described by the cage effects phenomenon and acoustic cavitation that is performed at high pressures and temperatures within a few seconds. Thus, this powerful technique can be considered as an excellent reaction media for economical and green approaches in organic functional group transformations, including conversions of alcohols to chemically important aldehydes [3-9]. In recent years, organic-inorganic hybrid porous coordination polymers, called Metal-Organic Frameworks (MOFs), have attracted significant attention as favorable materials owing to their potential applications in sensors [10,11], drug delivery [12–15], gas separation [16], catalysis [17–21], and photocatalysis [22–26]. MOF-based structures exhibit some special properties of both inorganic and organic materials, such as tunable pore sizes, high surface areas, flexibility, exposed active sites, the ease of process ability, and structural diversity. As an approach to improve the selectivity, polar functional groups, namely basic nitrogen-bearing groups including aromatic amines, heterocycles, and alkylamines, have been broadly incorporated into MOFs [27,28]. 2-Aminoterephthalic acid (H_2ABDC) has been widely used as an efficient organic building block for making open frameworks, such as NH_2−MIL-53, IRMOF-3, NH_2-UiO(Zr)-66, etc [29-34]. In such complex compounds, carboxylate groups of the deprotonated ABDC^{2-} ligand are the only participants in metal bonding. Whereas the replaced amino groups are not coordinators of the metal centers, they possibly function as binding sites [35]. Building unsaturated metal centers (or OMSs)

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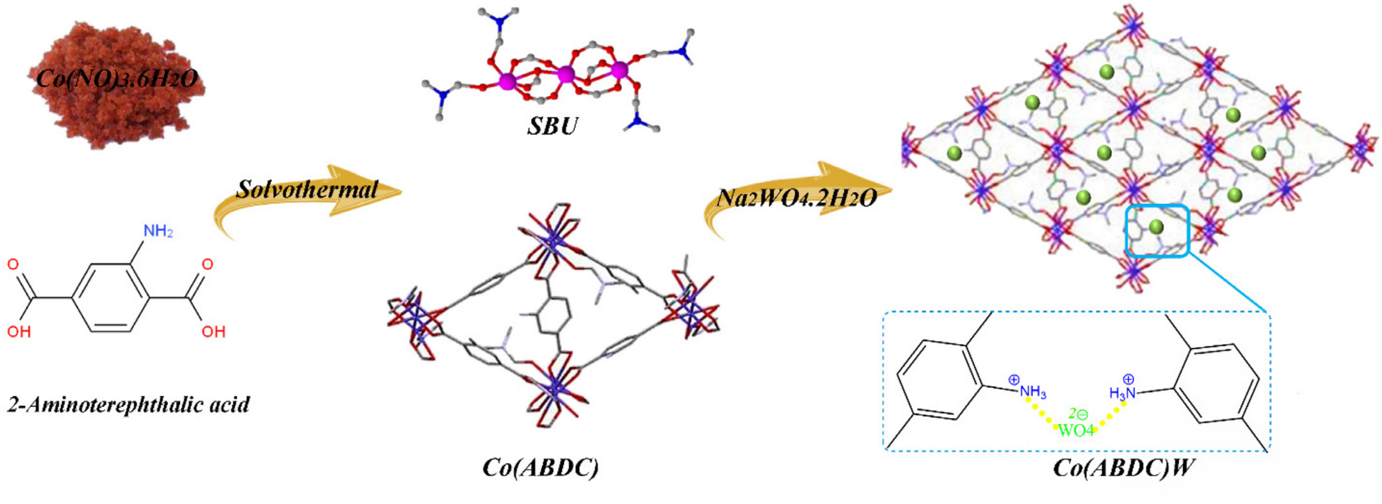


Fig. 1. Synthesis route of Co-ABDC/W MOF.

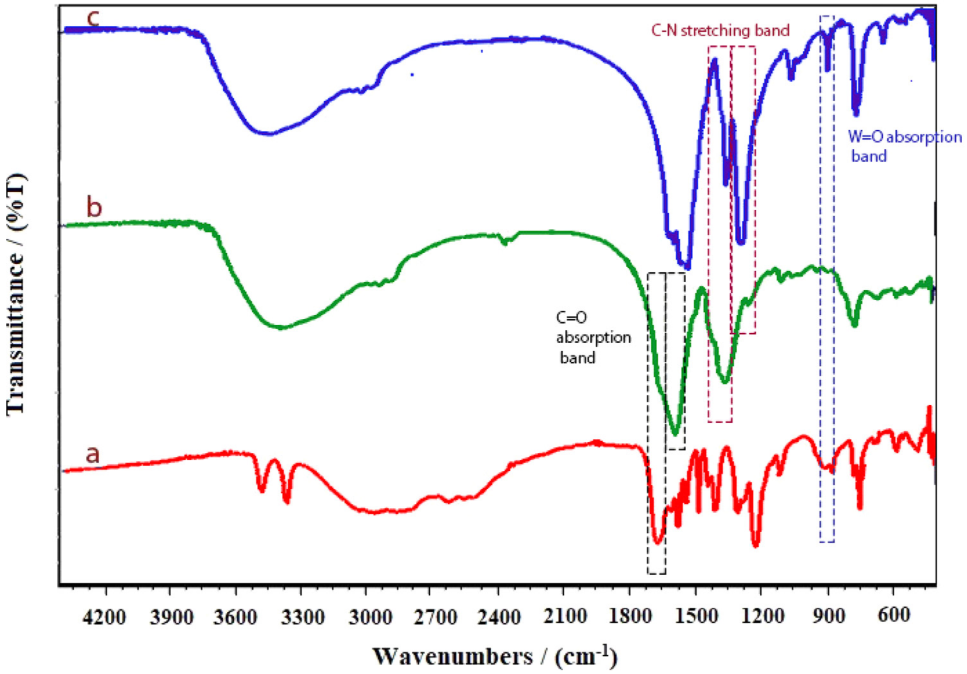


Fig. 2. FT-IR spectra of a) pure 2-Aminoterephthalic acid, and b) Co-ABDC and c) Co-ABDC/W MOF.

in the frameworks is another common approach for improving the selectivity and affinity of MOFs. These open metal sites are usually obtained upon the desolvation of MOFs, where the solvent molecules in the coordination of the metal centers are removed under vacuum and/or at the elevated temperatures [36-38]. Application of tungsten moiety aims to convert cyclohexene to adipic acid using sodium tungstate (Na_2WO_4). Diverse types of W-base systems have been extremely used due to the fact that they have high selectivity and activity in most oxidation processes, such as oxidation of sulfides to sulfoxide, halogenation of olefins, isomerization of alkenes, and oxidation of alcohols to aldehydes [39,40]. W-base systems are actuated by hydrogen peroxide as a green oxidant owing to the co-formation of water and large quantity of active oxygen. Homogenous W-based catalysts are associated with few notable weaknesses, such as reusability, recovery, the use of phase transfer catalysts, etc. Heterogenization of W-species onto the solid support has gained ground to surmount the mentioned challenges in recent years [41].

Taking the mentioned content into account, an affordable catalyst was prepared based on amino-functionalized MOF that was immobilized by tungsten aiming to oxidize alcohols to aldehydes and ketones under eco-friendly condition. Amino-functionalized MOF was synthesized using a solvothermal technique. Subsequently, it was mixed with $Na_2WO_4{\bullet}2H_2O$ and stirred for 24 h at 40°C until the solid violet precipitate was obtained which was denoted as an Amino-functionalized MOF/tungstate. In addition, selective and solvent-free oxidation of aromatic alcohols to the corresponding aldehydes were reported in the presence of H_2O_2 as an oxidant agent and Co(ABDC)/W catalyst under ultrasonic irradiation conditions at room temperature. To the best of our knowledge, this selective approach is the first report aiming to use MOF-based structure in conjunction with ultrasonic irradiation in the oxidation of alcohols.

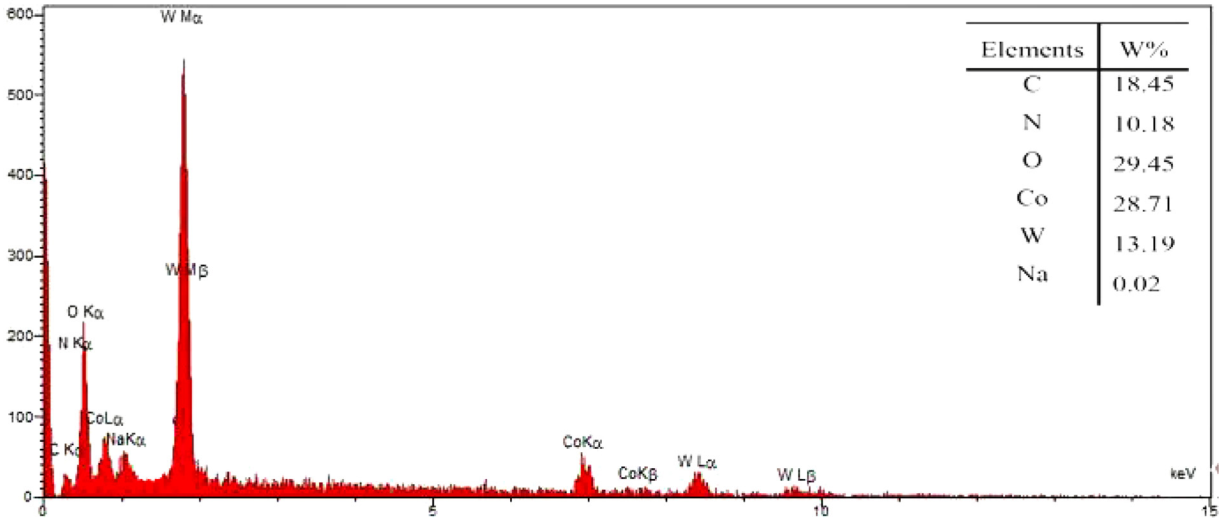


Fig. 3. EDS analysis of the Co-ABDC/W MOF.

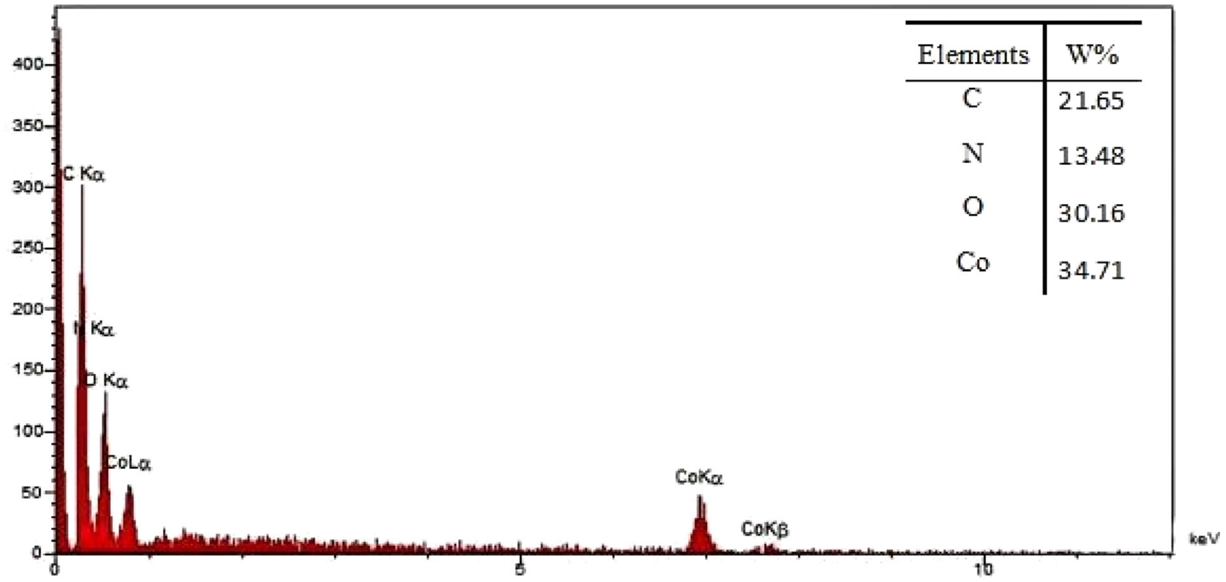


Fig. 4. EDS analysis of the Co-ABDC MOF.

2. Experimental

2.1. General

All solvents and reagents were purchased from Sigma Aldrich and Merck and utilized without further purification. FT-IR samples were prepared as KBr pellets and spectra were recorded on a PerkinElmer 1600 FTIR spectrometer. All products were confirmed by a GC manufactured by Teif Gostar Faraz Co., Iran. The powder diffractometer patterns were collected by ADVANCEX-ray with CuK radiation. Elemental analyses were obtained using a PerkinElmer analyzer. Thermal stability of heterogeneous MOFs was measured with a heating rate of 5 °C min^{-1} from 50 to 600 °C on a Perkin Elmer STA 6000 TGA. Field Emission Scanning Electron Microscopy (FE-SEM) imaging was performed on a Zeiss microscope with an attached camera. Ultrasonic irradiation was generated by a Digital Sonifier S-250D from Branson.

2.2. Synthesis of Co-ABDC/W

The catalyst was obtained according to the previously mentioned procedure [42]. The MOF was prepared through solvothermal reactions of 2-Aminoterephthalic acid (0.4 mmol) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \bullet 6H_2O$) (0.8 mmol) in the ethanol-DMF solution that was mixed in a 50 ml beaker. The reagents were stirred for 15 min and then transferred to a 40 mL Teflon-lined autoclave, and heated at 125 °C under autogenous pressure for 48 h. Dark violet solid was collected by centrifuge, washed three times with DMF, rinsed twice by methanol over 24 h, and dried at 80 °C in a vacuum oven. Finally, the resulting dark violet solid was added to 25 mL of saturated $Na_2WO_4 \bullet 2H_2O$. The mixture was stirred for 24 h at 40 °C. The precipitated violet solid was collected by centrifuge, washed by methanol/DMF, and dried in a vacuum oven at 60 °C.

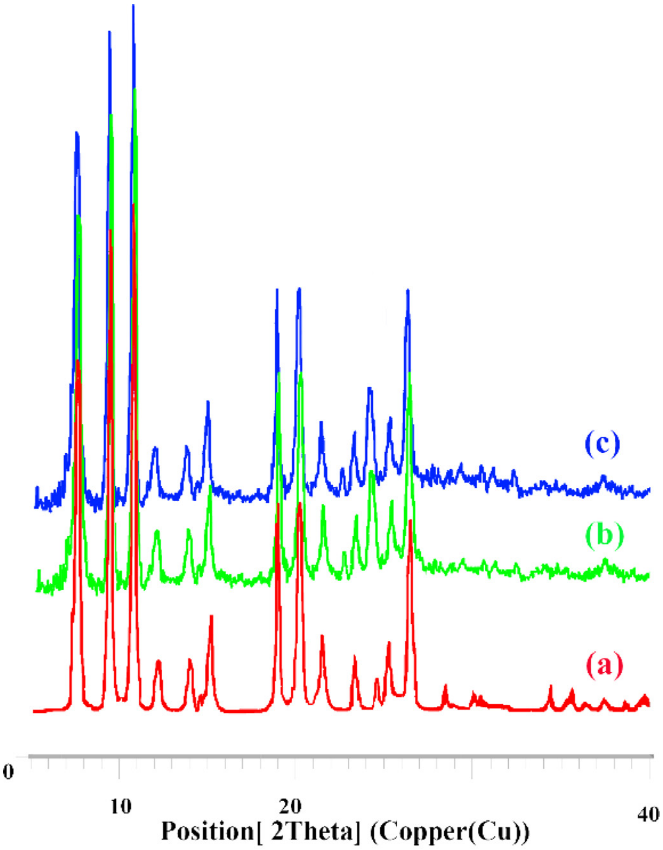


Fig. 5. Comparison of XRD patterns of synthesized a) Co-ABDC (green), b) Co-ABDC/W (blue), and simulation (red).

2.3. Ultrasonic oxidation procedure

A mixture of benzyl alcohol (1 mmol), aqueous hydrogen peroxide, and Co-ABDC/W as heterogeneous catalysis (0.01 g) was sonicated in an ultrasonic bath (constant frequency) at 25 °C by circulating water. At the end of the oxidation, the mixture was diluted by adding ethyl acetate (3 × 15) to separate the product from the catalyst. The MOF was then washed and to be reused directly for a new procedure, without further purification.

The catalytic performance of the catalyst was calculated in terms of conversion of benzylic alcohols (%) and yield/selectivity (%) to the product according to the following equations:

$$\text{Conversion}\ (\%) = \frac{\text{Initial moles of benzylic alcohol} - \text{remaining moles of benzylic alcohols} \times 100}{\text{Initial moles of benzylic alcohols}}$$

$$\text{Aldehyde yield}\ (\%) = \text{Moles of formed aldehydes} \times 100 / \text{Initial moles of alcohols}$$

$$\text{Aldehyde selectivity}\ (\%) = \text{Aldehyde yield} \times 100\ /\text{conversion}$$

3. Results and discussion

In this work, $[Co_3(ABDC)_3(DMF)_4]$ was first synthesized from the reaction of 2-Aminoterephthalic acid and cobalt nitrate hexahydrate by a solvothermal method according to the previously mentioned procedure. According to literature, Co-ABDC coordination polymer is not only isostructural but also based on a trinuclear cobalt cluster [37]. As it can be seen in Fig. 1, the trinuclear $[Co_3(CO_2)_6]$ secondary building unit is connected to six ABDC ligand to produce a two-dimensional structure. The Co-ABDC was produced after removing coordinated DMF molecules and then tungsten was immobilized on MOF support. The MOF was then characterized using different techniques.

3.1. Characterization of Co-ABDC/W MOF

FT-IR spectroscopy is a powerful tool to identify the functional group of organic compounds. FT-IR spectra of amino-functionalized metal-organic framework (Fig. 2b) exhibited a significant difference compared to that of pure 2-Aminoterephthalic acid (Fig. 2a). Two dominant peaks that are appeared between 3300–3600 confirmed the existence of symmetric and asymmetric stretching vibrations of the NH_2 group that are shown in Fig. 2a. The peaks in the range of 1400 cm^{-1} and 1600 -1500 cm^{-1} can be respectively ascribed to the asymmetric and symmetric stretches of the carboxylate group (Fig. 2a). The deprotonation of COOH groups in 2-Aminoterephthalic acid after reacting with metal ions was validated as strong absorption bands that are present at 1650 cm^{-1} and at the same time the absorption bands that are absent at around 1700 cm^{-1}. The C-N stretching band of Co-ABDC (Fig. 2b) appears at 1340 cm^{-1}. The mentioned band for Co-ABDC/W (Fig. 2c) is shifted to a lower frequency (1275 cm^{-1}) owing to complexation with the tungstate. Lastly, a peak emerging at 890 cm^{-1} in c spectrum can be ascribed to W=O (Fig. 2c) [43].

EDS analysis identifies the purity of materials by qualitative detection of elements. EDS spectrum of Co-ABDC/W (Fig. 3) presents the presence of Co, N, O, C, and W elements in their specified energy which confirms the purity of the product.

As shown in Fig. 4, all mentioned elements exist in EDS analysis of the Co-ABDC except W.

The crystalline phase purity of the synthesized Co-ABDC/W MOF was analyzed by X-Ray Powder Diffraction (XRD). As shown in Fig. 5, the characteristic diffraction peaks of the prepared sample are in good agreement with the theoretical patterns (Fig. 5a). Moreover, the crystalline structure of the as-prepared Co-ABDC is similar to the pattern reported by Ying Yang et. Al [42]. The powder XRD patterns of Co-ABDC/W confirm that this material has isoreticular frameworks. As can be observed from Fig. 5, the powder XRD patterns of both Co-ABDC (5b) and Co-ABDC/W (5c) have identical characteristics which confirm that the complexation with tungstate has no effect on the crystalline structure.

To study the morphology of Co-ABDC/W MOF and how to connect tungstate to MOF, the FE-SEM was applied. As expected, the SEM micrograph confirms the achievement of crystalline material (similar to rhombus shape) (Fig. 6). The FE-SEM graphs reveal the as-prepared catalyst in different magnificent. As it can be seen from Fig. 6C, the particle size of the as-prepared catalyst was measured to be between 24.84 to 63.53.

The comparative study on the TGA plots of the Co-ABDC/W (blue) and Co-ABDC (green) are shown in Fig. 7. All two samples were thermally stable up to 300 °C. A first weight losses of ≈ 1–3% are observed at below 200 °C, suggesting the evaporation of surface-adsorbed solvents and coordinated DMF. Co-ABDC shows a fast weight loss of up to 300 °C (around 350 °C for 60% weight loss), indicating the rapid decomposition of structure. While the Co-ABDC/W weight loss (>40%) occurred between 400 °C to 450 °C, the decomposition of Co-ABDC/W happened at a higher temperature. It was assumed that a difference in the network forces of the MOFs or morphology may explain the difference between the obtained thermal stability of samples.

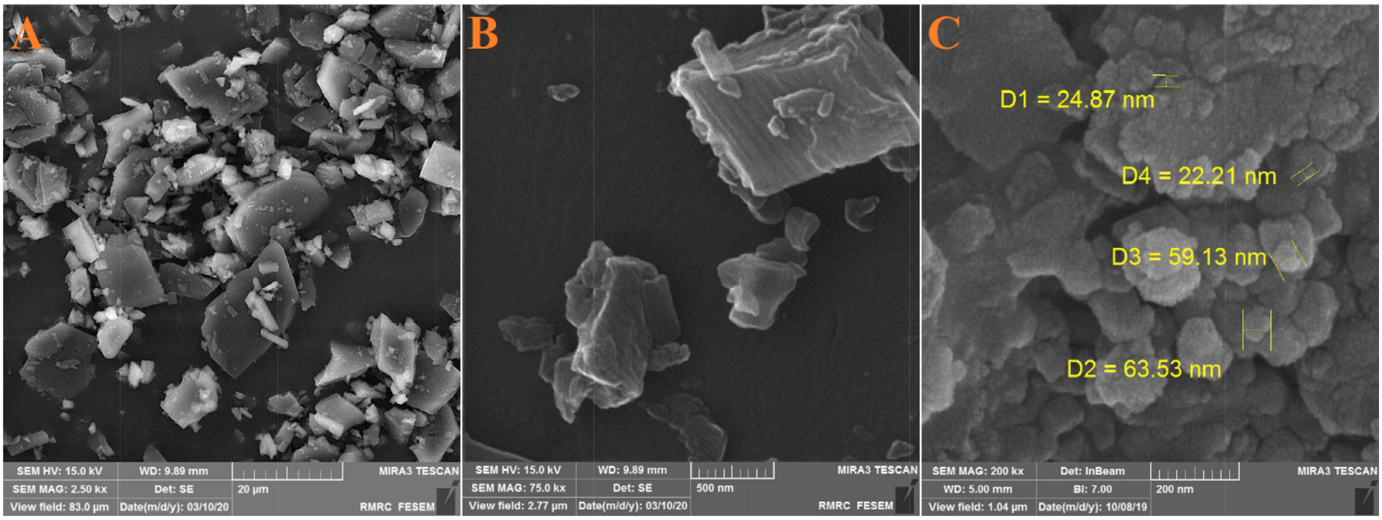


Fig. 6. FE-SEM micrograph of the Co-ABDC/W MOF in different magnificent.

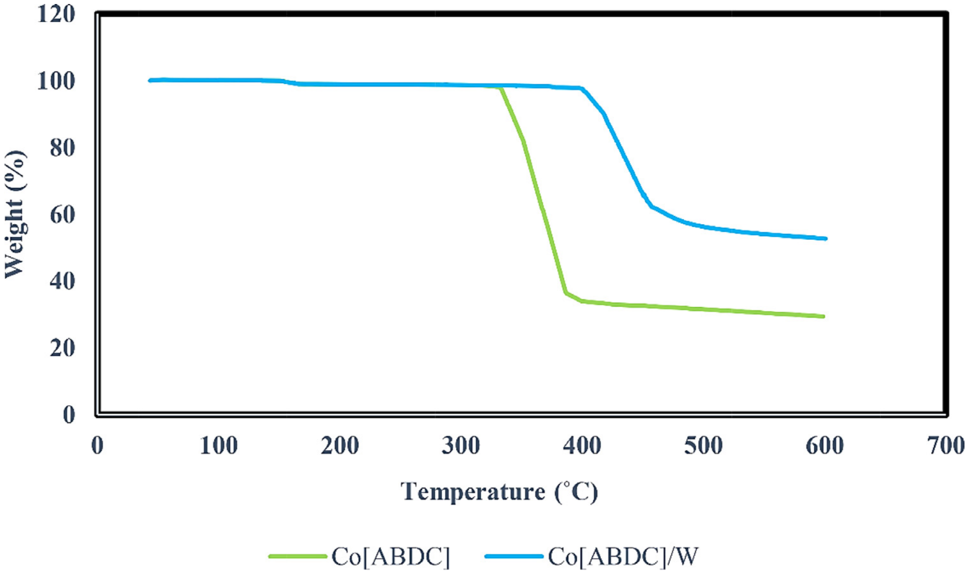


Fig. 7. TGA curves of Co-ABDC/W and Co-ABDC measured in air.

3.2. Catalytic sonochemical oxidation of benzylic alcohols

Direct sonochemical oxidation of alcohol under solvent-free condition as a green process requires an efficient catalyst to provide the activation of alcohol and oxygen molecules. Therefore, we checked the activity of the prepared catalyst for selective oxidation of benzyl alcohol using H_2O_2 as the oxidant under mild conditions. The conditions in solvent-free oxidation reactions were optimized to explore the performance of the catalyst. A pilot test was conducted with benzyl alcohol in the presence of various amounts of Co-ABDC/W MOF catalyst under ultrasonic irradiation to afford benzaldehyde. It is worth mentioning, sonoxidation of benzyl alcohols could not proceed in the absence of either catalyst or H_2O_2 (Fig. 8). It was found that the optimum amount of catalyst was about 0.01 g to afford 100% yield at 25°C after 5 min based on the results of gas chromatography analysis. Then, the influence of hydrogen peroxide concentrations was investigated on the ultrasonoxidation. Benzaldehyde (model substrate) yield increased from 25% to 100% when the H_2O_2/ substrate molar ratio increased from 0.5 to 1 under solvent-free sonication irradiation and decreased to 65% at 3 molar equivalents of H_2O_2 (Fig. 8). Below 1 molar equivalent of oxidant, the limited concentration of oxidizing moieties seems to promote high selectivity by limiting the over-oxidation phenomena [44]. Increasing the amount of catalyst and oxidant led to an increase in the conversion of benzylic alcohols, while a decrease occurred in the selectivity because of a little over-oxidation to yield by-products, such as carboxylic acids.

The catalytic performance of Co-ABDC/W was compared with other catalysts to investigate the need for the present catalyst for the oxidation of alcohols. To this end, a pilot reaction was done in the presence of different catalysts, such as Lewis acids, Co_3O_4 NPs, MWCNTs/TiO_2, Co-ABDC, and Co-ABDC/W (Table 1). The yields of conversions in the rest of the cases were lower or contained side products. An experiment was also carried out in the absence of a catalyst. The yield of the reaction in this case was very traced after 45 min. A comparison between the last two rows (Table 1) clearly demonstrates the power of activated tungstate anion during sonochemical oxidation protocol. Sonication conditions had a significant role in this process. In the absence of ultrasonic irradiation, (stirring/ grinding/ classical heating) no considerable yields were observed. The optimization of the ultrasonic instrument was done within the power of 100–300 W and the frequency range of

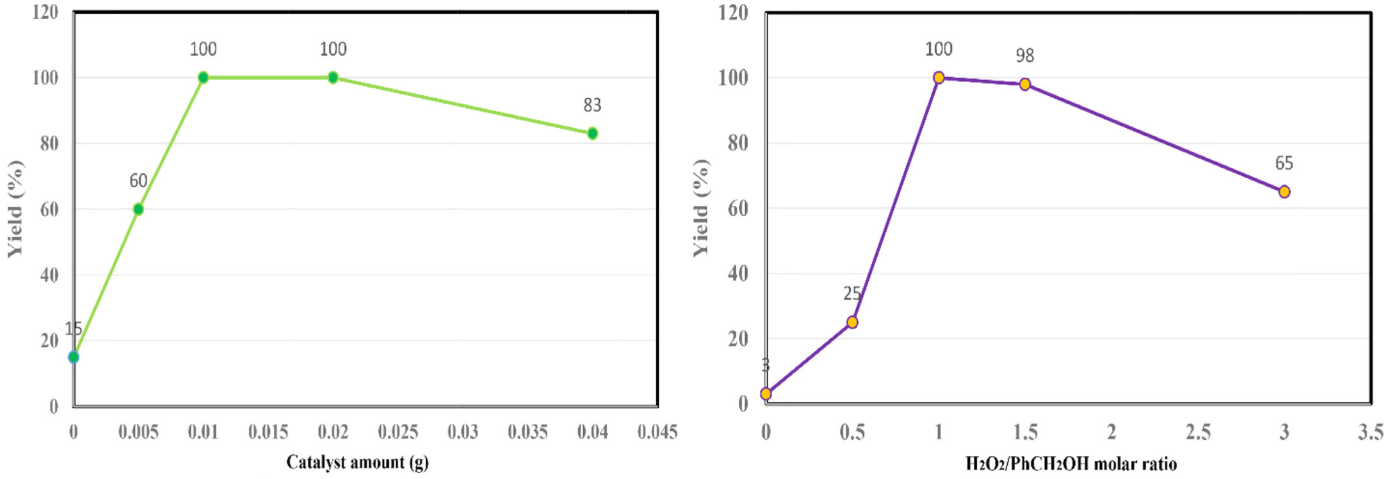


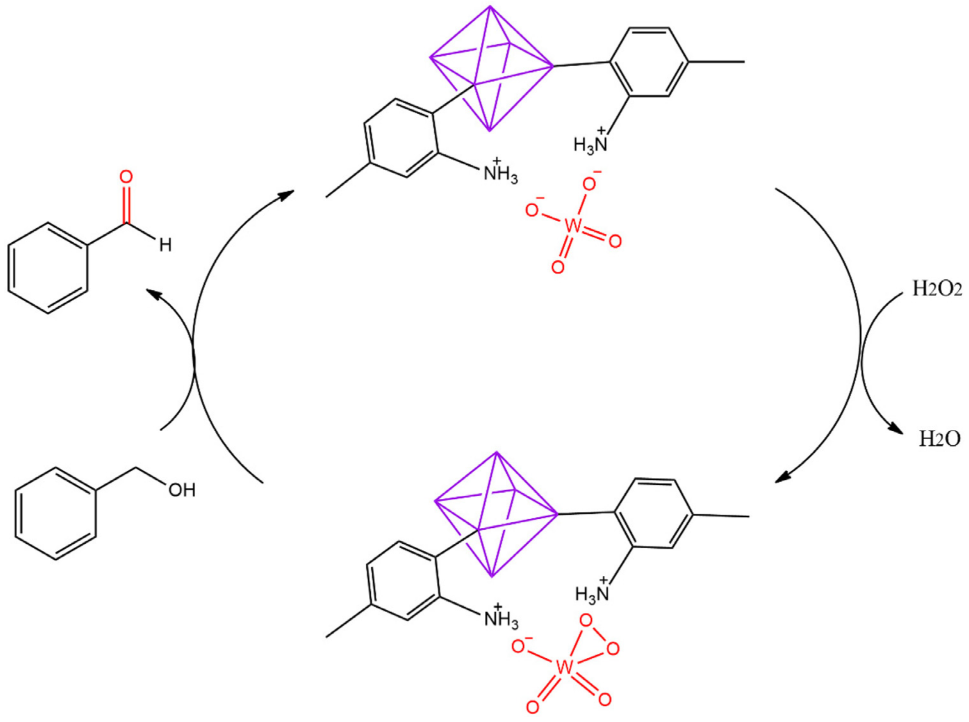
Fig. 8. Oxidation of $PhCH_2OH$ as a function of catalyst amount (g) and $H_2O_2/PhCH_2OH$ molar ratio under US irradiation (40 kHz, 100 W) at 5 min.

Table 1
Optimization of various reaction conditions on the model reaction[a].

Entry	Conditions	Time (min)	Yield [b] (%)	Ref.
1	Stirring, r.t.	45	Trace	This work
2	Ultrasound, r.t.	5	15	This work
3	Co-ABDC/W, stirring, r.t.	30	55	This work
4	H_2SO_4, ultrasound, r.t.	30	38	This work
5	HCl, ultrasound, r.t.	30	32	This work
6	Co_3O_4 NPs, ultrasound, r.t.	30	68	This work
7	MWCNTs/TiO_2, ultrasound, r.t.	15	100	[45]
8	Co-ABDC, ultrasound, r.t.	20	100	This work
9	Co-ABDC/W, ultrasound, r.t.	5	100	This work

[a] Benzyl alcohol (1 mmol), H_2O_2 (15% Wt.), catalyst (0.01 g), ultrasonic: 40 kHz, 100 W.

[b] Conversion yield



Scheme 1. A possible reaction mechanism.

Table 2
Solvent-free sonoxidation of various alcohols[a].

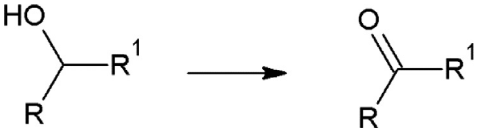
Entry	R	R^1	Time (min)	Yield [b] (%)	Selectivity (%)	
1	2-Methoxyphenyl	H	))))US	9	96	100
			Δ	180	90	95
2	4-Methoxyphenyl	H	))))US	7	100	100
			Δ	165	93	96
3	2-Chlorophenyl	H	))))US	6	98	99
			Δ	155	92	97
4	4-Chlorophenyl	H	))))US	5	100	100
			Δ	140	97	100
5	4-Nitrophenyl	H	))))US	7	96	100
			Δ	150	88	96
6	2-Nitrophenyl	H	))))US	8	95	100
			Δ	160	89	99
7	4-Bromophenyl	H	))))US	12	92	98
			Δ	230	75	97
8	Phenyl	H	))))US	5	100	100
			Δ	200	98	100
9	Phenyl	Methyl	))))US	8	90	100
			Δ	185	85	100
10	Phenyl	Ethyl	))))US	8	90	100
			Δ	160	87	99
11	Phenyl	Phenyl	))))US	10	90	100
			Δ	205	89	97
12	4-Chlorophenyl	Phenyl	))))US	15	85	99
			Δ	210	83	96
13	4-Chlorophenyl	4-Chlorophenyl	))))US	20	84	99
			Δ	225	79	97
14	4-Methoxyphenyl	Phenyl	))))US	10	91	100
			Δ	190	89	99
15	4-Methoxyphenyl	4-Methoxyphenyl	))))US	9	92	100
			Δ	190	92	100

[a] Reaction conditions: alcohol (1 mmol), H_2O_2 (15% wt), and catalyst (0.01 g). Ultrasonic irradiation: 40 kHz, 100 W at room temperature or under the conventional heating condition at 60 °C.

[b] The conversion yield was based on GC analyses.

30–70 kHz. As a result, the best data were obtained in 40 kHz frequency and 100 W power. Moreover, it can be concluded that the existence of the MOF catalyst and ultrasonic irradiation could synergistically affect one another for selective and significant promotion of the oxidation reactions.

To investigate the domains and limitations of Co-ABDC/W MOF, various substituted benzyl alcohols with both electron-donating (OCH_3) and electron-withdrawing (Cl, Br, NO_2) were oxidized under optimized conditions. The preadsorption of the various substrates on the surface of Co-ABDC/W MOF was modified by the steric arrangement of functional group and substitution. The mentioned hypothesis was partially confirmed by the presence of a steric effect in the ortho and para isomers of chlorobenzyl alcohols, methoxybenzyl alcohols, and nitrobenzyl alcohols with a reactivity trend of ortho $<$ para (Table 2). To expand the applicability of the fabricated Co-ABDC/W MOF for selective oxidation, sonocatalytic oxidation of various alcohols other than primary benzyl alcohols was examined. As shown in Table 2, prepared MOF was also effective in oxidation of the secondary aromatic alcohols (Table 2, entry 9–15) to corresponding ketones. In most oxidations cases, secondary aromatic alcohols had lower yields and longer reaction times compared to that of the primary benzylic substrate. It might due to the larger steric hindrance of the aryl groups. Besides, the secondary benzylic alcohols possessing electron-donating substituents (methoxy-) on the aromatic ring were oxidized to the corresponding ketones with higher conversions (Entries 14,15). This method proceeded quite cleanly under mild conditions, without undesirable side reactions under ultrasonic irradiation (40 kHz, 100 W). The efficient advancement of the reaction in all of the examined cases in the presence of the catalyst is presented in Table 2.



In summary, based on the empirical results, it can be stated that the ultrasound irradiation can remarkably improve the yield of the reactions as well as decreasing the reaction times in the presence of H_2O_2 and Co-ABDC/W MOF as a catalyst compared to a conventional heating method. It should be mentioned that the Co-ABDC/W MOF is nontoxic, stable to moisture or air, and very active. Another advantage of this efficient catalyst is its high selectivity. Furthermore, it can be recovered by simple separation and reused in reactions for at least five runs (Fig. 10) with only a bit attenuation of activity. According to the XRD pattern of Co-ABDC/W MOF (Fig. 9), the crystalline structure was maintained after 5 cycles of reuse. Therefore, the slight attenuation is mainly because of the loss of Co-ABDC/W MOF after centrifugation.

According to the successful studies of the plausible mechanism for the oxidation process in the presence of transition metals [38,46], procreation of $W(O_2)\,O_3$ from the reaction of tungstate anion of the catalyst with H_2O_2 is the proposed reaction mechanism. The activated catalyst can transfer an oxygen molecule to the substrate. The oxidation procedure occurs and then the aldehyde product is produced from the benzylic alcohol substrate. After this step and passing the active oxygen molecule, the WO_4 anion regenerates (Scheme 1).

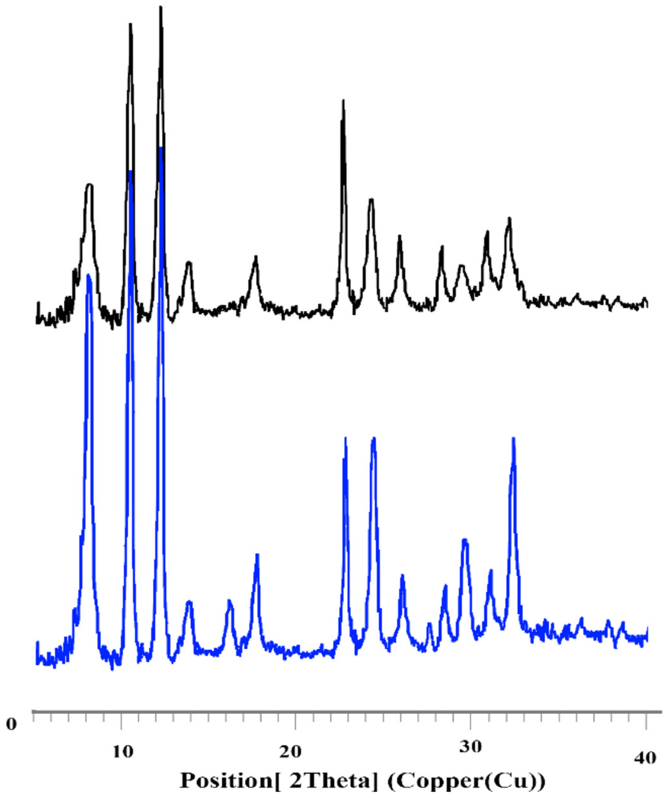


Fig. 9. Comparison of XRD patterns of the prepared Co-ABDC/W MOF (blue) and after 5 runs (black).

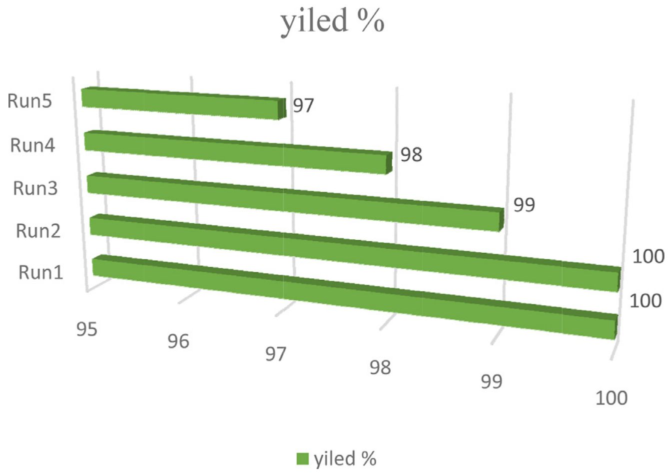


Fig. 10. Recycling experiment of the Co-ABDC/W MOF catalyst.

4. Conclusions

The main challenge of this study was to conduct the catalytic ultrasonoxidation of benzylic alcohols to the corresponding aldehydes under milder and greener reaction conditions than those that were used in the literature. In this regard, a new amino-functionalized MOF was introduced as a heterogeneous catalyst with OMSs. Ultrasound mediated selective oxidation demonstrated to be more effective than the reaction performed under conventional heating due to synergistic effects between the ultrasound, H_2O_2, and the solid catalyst. The powder XRD patterns confirmed that the complexation with tungstate has no effect on the crystalline structure while the TGA plots revealed a significant difference. This powerful and green sonochemical method for the oxidation of synthetic compounds presented some significant advantages, such as easy workup procedure, readily available precursors, recyclability of the heterogeneous catalyst, high atom economy, short reaction times, and excellent conversion yields according to the green chemistry principles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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