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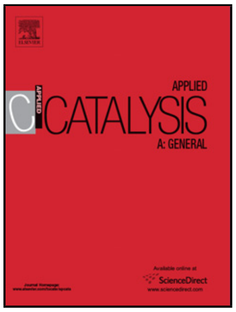

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$Cu_3(BTC)_2$ Catalyzed Oxidation of Silane to Silanol using TBHP and Water as Oxidants

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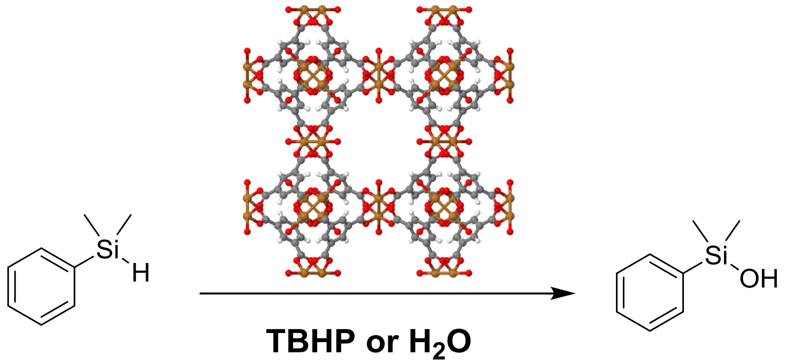
Graphical Abstract



Highlights

- To develop a simple and convenient water stable catalyst for the oxidation of silanes to silanols in replacing precious noble metal based catalysts.
- To avoid the use of strong oxidizing agents such as permanganate, peroxides, ozone, and peracids.
- To develop a highly stable and reusable catalyst for the oxidation of silane to silanol in water.

Abstract

In the present work, a series of metal organic frameworks are examined for the conversion of Si-H to Si-OH using either t-butylhydroperoxide (TBHP) or water as oxidants. The reaction is optimized using dimethylphenylsilane (**1**) as a model substrate. It is observed that $Cu_3(BTC)_2$ (BTC: 1,3,5-benzenetricarboxylate) exhibits a comparable activity with Zr(BDC) (BDC: 1,4-benzenedicarboxylate) but however the activity of Fe(BTC) is lower than $Cu_3(BTC)_2$ using TBHP as oxidant. On the other hand, the reaction of **1** with water in the presence of $Cu_3(BTC)_2$ as a catalyst showed complete conversion with 99% selectivity to the corresponding silanol while other MOFs like Fe(BTC) and Zr(BDC) are inactive under identical reaction conditions. A series of control experiments indicate that Cu^{2+} is essential to convert **1** to **2** under the present experimental conditions. Further, Cu^{2+} in $Cu_3(BTC)_2$ acts as redox centre while the use of TBHP whereas it behaves as a Lewis acid using water as oxidant. High conversion and selectivity is observed for all the silanes studied under the present experimental conditions. The catalyst stability is monitored by powder XRD, FT-IR and SEM images and observing no structural deterioration of $Cu_3(BTC)_2$ either in TBHP or water as oxidants. Furthermore, hot filtration test indicated the absence of copper under the present reaction conditions, thus confirming the stability of $Cu_3(BTC)_2$.

Keywords: Metal Organic Frameworks; TBHP; Silane oxidation; Si-H activation; Water

1. Introduction

Silanols are compounds containing Si-OH bonds and are silicon analogues of alcohols [1], which have found important applications in various fields [2], especially in the production of silicon-based polymeric materials [3]. Furthermore, several organosilanols have shown to exhibit bioactivity [4, 5] and some of them were applied as structural components in the transition-state analogues of metalloprotease inhibitors [6, 7]. In addition, silanols are useful synthons in various fields of organic synthesis as well as in materials science [8-11]. In organic synthesis, they have been employed as a nucleophilic coupling partner in metal catalyzed carbon-carbon cross-coupling reactions [12-14], hydrogen bond donors in organocatalysis [15-17] and directing groups in C-H bond activation [18-21]. A variety of procedures of have been developed for the synthesis of silanols which include hydrolysis of chlorosilanes [22], oxidation of organosilanes with stoichiometric amounts of oxidants[23] and treatment of siloxanes with alkali metal reagents [24]. However, some of the main issues associated with these methods are limited scope, formation of toxic by-products and generation of disiloxanes as side products consequent from the condensation of silanols. On the other hand, catalytic oxidations of the Si-H bond of organosilanes have been reported with Ni, Cr, Rh, and Cu complexes [25-28]. However, these protocols showed a rather limited selectivity to certain substrates and they produce disiloxanes in high amounts in many cases. In order to overcome these drawbacks, there is a huge demand to develop an efficient catalyst for the conversion of silanes into silanols.

The development of efficient synthetic methods, which minimize environmental problems, is a great challenge for chemists in both industrial and academic research. In this context, homogeneous transition metal catalysts have emerged to meet these requirements mentioned above, but, however their use accompany with a difficulty of residual metal impurities in the final products and they suffer from reusability standpoint. Subsequently, heterogeneous catalytic systems have emerged as potential alternatives, because of the inherent operational advantages such as ease of handling, separation and recovery of the catalyst from the reaction mixture for reusability [29]. However, one of the major issues of heterogeneous catalysis are gradual leaching of transition metals from the solid supports [30, 31].

During the last few decades, metal organic frameworks [32, 33] (MOFs) have emerged as potential candidates for variety of applications in the field of gas storage [34], gas separation [35], drug delivery [36], sensor[37] and heterogeneous catalysis [38]. MOFs are a class of crystalline porous solid whose structure is constructed from metal nodes or cluster interconnected by rigid bi- or multipodal organic linkers [39-41]. They possess large surface area, high porosity, structural diversity and high metal density [42]. In this regard, $Cu_3(BTC)_2$ is one of the well-known MOF, which is composed from dimeric cuprate tetra carboxylate units [43]. Furthermore, $Cu_3(BTC)_2$ has been used as heterogeneous catalysts for a wide range of reactions including oxidation of benzylic alcohol [44], cyanosilylation of benzaldehyde [45], ring opening of epoxide [46], benzylic oxidation [47], Knoevenagel condensation [48] and dehydrogenative coupling of silane [49]. The above reactions suggested that $Cu_3(BTC)_2$ is a stable catalyst in promoting these organic transformations. However, certain MOFs showed poor stability in polar solvents like water and DMF and in particular with water due to their high dielectric constant separating ion-pairs can in principle cause deterioration of the crystal structure [50]. Hence, it is always challenging to develop a catalytic system for organic transformation using water as solvent or oxidant. Hence, the present study aims to report the activity of $Cu_3(BTC)_2$ as a stable and an efficient reusable heterogeneous catalyst for oxidation of silanes to silanols either in water or with TBHP as oxidants. On the other hand, the activity of $Cu_3(BTC)_2$ is compared with analogous heterogeneous solid MOFs. Moreover, the stability of $Cu_3(BTC)_2$ is also surveyed under these experimental conditions. One of the main objectives of the present work is to develop a simple and convenient catalyst in replacing strong oxidizing agents that have been frequently used for the conversion of silanes to silanols such as permanganate, peroxides, ozone, and peracids [51-53]. However, these protocols usually lead to significant amounts of byproducts, such as siloxanes that are produced from silanol condensation. In addition, the present work could be an alternative protocol for the replacement of the use of precious noble metals like gold, silver, palladium nanoparticles [54-56] and bimetallic nanoparticles [57] which have been used as catalyst for the oxidation of hydrosilanes in the presence of water as oxidant.

2. Experimental

2.1 Materials

$Cu_3(BTC)_2$ and Fe(BTC) were purchased from Sigma Aldrich under the commercial trade Basolite C300 and Basolite F300 respectively. Zr(BDC) was synthesized by following the protocol reported in an earlier precedent [58]. A dimethylphenylsilane, triphenylsilane and diphenylsilane used in the present study were purchased from Sigma Aldrich and used as received. *tert*-Butylhyroperoxide and acetone were purchased from Sigma Aldrich and used as received. Tetrahydrofuran (THF), ethyl acetate and sodium sulfate were also purchased from Sigma Aldrich and used as received.

2.2 Instrumentation

Powder XRD diffraction patterns were measured in the refraction mode in a Philips X'Pert diffractometer using the CuKα radiation (λ = 1.54178 Å) as the incident beam, PW3050/60 (2 theta) as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, incident mask fixed with 10 mm. PW3123/10 for Cu was used as a monochromator. PW3373/00 Cu LFF was used as X-ray tube with power scanning of 45 kV and 40 mA current. The sample powder was loaded into a holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 2^o and 70^o with the scan rate of 0.02^o/s. Scanning electron microscope (SEM) studies were performed using a Hitachi S-3000H scanning electron microscope.

2.3 Reaction procedure

In a typical experimental procedure, 25 mg of $Cu_3(BTC)_2$ was charged into a 50 mL round bottom flask followed by the addition of 1 mmol of silane and 3 mmol of TBHP. This reaction mixture was stirred at 60 ^oC for 20 h. The progress of the reaction was monitored by gas chromatography and after completion of the reaction, the mixture was washed twice with acetonitrile and filtered. Then, the product is analyzed by gas chromatography for its purity and selectivity. Conversion and selectivity were determined by Agilent gas chromatography using internal standard method.

2.4 Reaction procedure using water as nucleophile

Typically, 25 mg of $Cu_3(BTC)_2$ was loaded into a 50 mL round bottom flask following the addition of 1 mmol of silane, 20 mmol deionized H_2O and 1 mL of THF. This reaction mixture was stirred at 65 ^{o}C for 4 h. It was observed that the reaction mixture turns from blue to brown and returned back to original colour after 4 h with the evolution of hydrogen gas. The reaction progress was monitored by gas chromatography and after completion of the reaction, the mixture was extracted with ethyl acetate followed by acetonitrile, filtered and then dried with sodium sulfate. Then, the product is analyzed by gas chromatography for its purity and selectivity. Conversion and selectivity were determined by Agilent gas chromatography using internal standard method. The same procedure is followed for the reusability experiments.

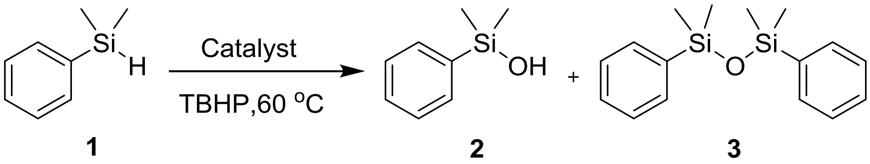
3. Results and Discussion

3.1. Structural aspects of MOFs

The crystal structure of Fe(BTC) is constituted between Fe(III) as a nodal metal ion and tripodal BTC as ligand. It is believed that the crystal structure of Fe(BTC) resembles with MIL-100(Fe) which is an iron(III) carboxylates built up from trimers of iron octahedra sharing a common vertex μ_3-O. These trimers are linked by the BTC ligands in such a way that this leads to the formation of hybrid supertetrahedra thus resulting in two types of mesoporous cages of free apertures of around 25 and 29 Å, accessible through microporous windows of around 5.5 and 8.6 Å. The BET surface area of Fe(BTC) was 1300 m^2/g. The second MOF in the present work is $Cu_3(BTC)_2$ whose crystal structure is constituted by the clusters of two Cu(II) ions coordinated with four BTC ligands defining a paddle-wheel building unit that acts as a structural node held in place by the tripodal BTC linkers. It has a surface area around 1050 m^2/g with 11, 16 and 6 Å pore dimensions. Furthermore, the crystal structure of UiO-66 [Zr(BDC)] is constructed between cationic $Zr_6O_4(OH)_4$ nodes formed in situ via hydrolysis of $ZrCl_4$ and BDC linkers with a cubic framework having high crystallinity. The BET surface area and pore dimensions of Zr(BDC) is 950 m^2/g and 8.4, 7.4 Å respectively.

3.2. Oxidation of silanes with TBHP

In the initial stage of our study, dimethylphenylsilane (**1**) was chosen as a model substrate for the conversion of silane to silanol (Scheme 1) using TBHP as oxidant and the attained results are given in Table S1. The reaction was optimized with respect to the concentration of TBHP and observing that the conversion of **1** increased gradually by increasing TBHP from 1 to 3 mmol in the presence of $Cu_3(BTC)_2$ as solid catalyst at 60 °C (Figure 1, Table S1). The maximum conversion of **1** was achieved to be 52, 92 and 96% with 1, 2 and 3 mmol of TBHP as oxidant, respectively (Table S1). Therefore, further studies were performed with 3 mmol of TBHP as oxidant. In contrast, $Cu_3(BTC)_2$ afforded 20% conversion of **1** with complete selectivity of **2** at room temperature after 20 h (Table S1).



Scheme 1. Oxidation of silane into silanol using TBHP or water as oxidant in the presence of MOFs as heterogeneous solid catalysts.

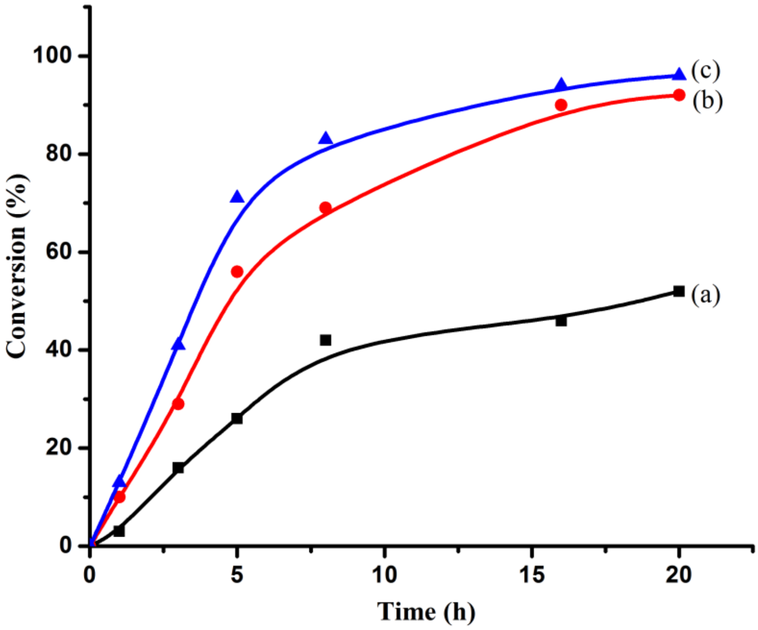
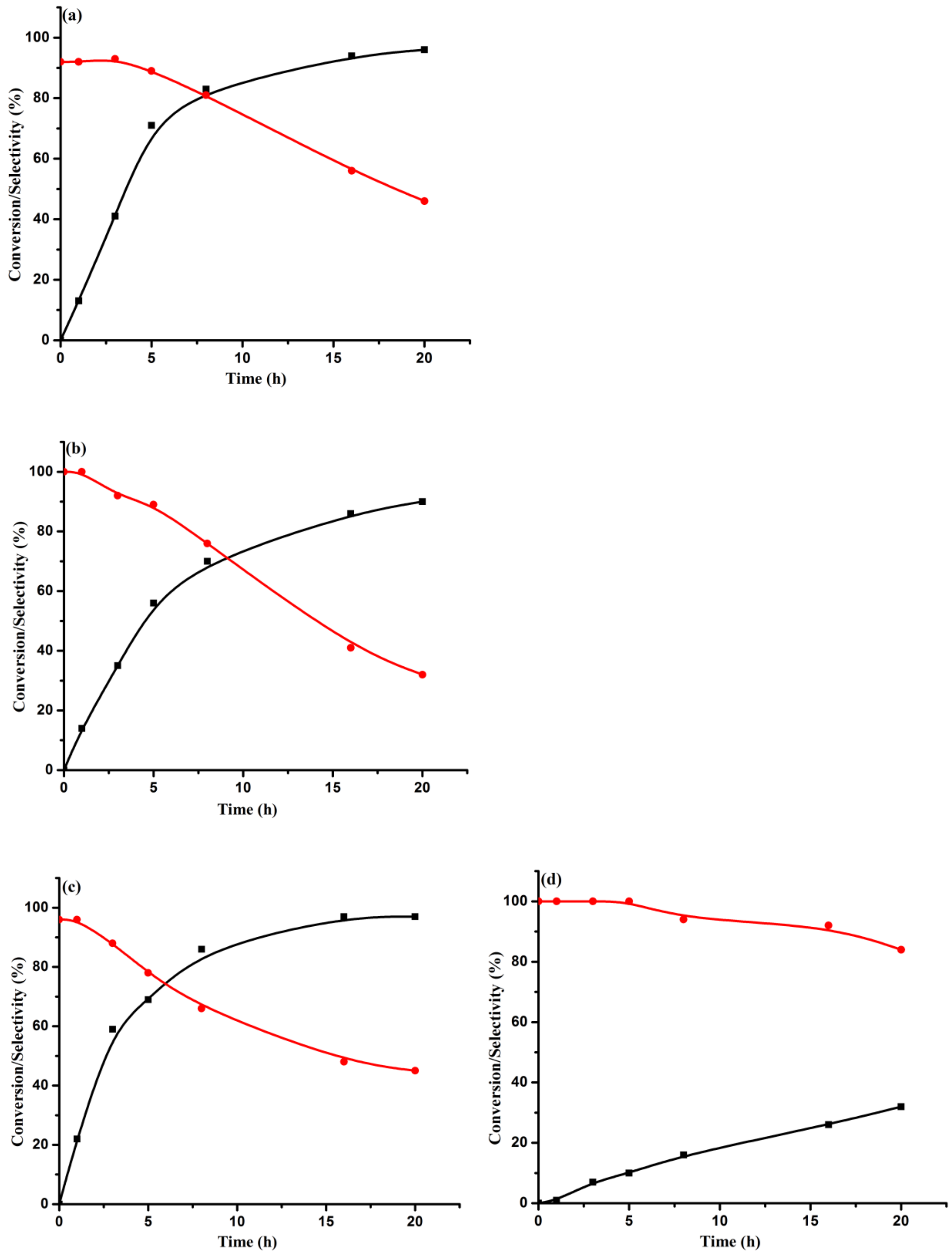


Figure 1. Time conversion plot for the conversion of **1** using $Cu_3(BTC)_2$ as heterogeneous solid catalyst with (a) 1, (b) 2 and (c) 3 mmol of TBHP as oxidant. Reaction conditions: **1** (1 mmol), TBHP (mmol), $Cu_3(BTC)_2$ (25 mg), 60 °C.

After optimizing the concentration of TBHP with $Cu_3(BTC)_2$ for the oxidation of **1** to **2**, a series of MOFs were studied as heterogeneous solid catalysts which include, Fe(BTC) and Zr(BDC) under the optimized reaction conditions. The observed results are given in Table S2. A maximum conversion of **1** was achieved to be 96, 90 and 97% using $Cu_3(BTC)_2$, Fe(BTC) and Zr(BDC) as catalysts, respectively, after 20 h with 3 mmol TBHP as oxidant at 60 °C. The time conversion plots for the conversion of **1** to **2** using different catalysts are given in Figure 2. On the other hand, a blank control experiment in the absence of catalyst showed 32% conversion of **1** after 20 h under identical reaction conditions, thus clearly establishing the role played by the MOFs in promoting the oxidation of **1** to **2**. In all these cases, it was observed that the selectivity of **2** is much higher in the initial reaction time, but, however, the formation of **3** is noticed upon reaction progress resulting from the condensation of **2**, which is predominant along with reaction time (Figure 2). It has been reported that $Cu_3(BTC)_2$ can convert **1** to the corresponding siloxane [59] and thus, in the present case, it is believed that self-condensation of **2** occurs at long reaction time thus reducing the selectivity of **2**. In order to understand the superior activity of $Cu_3(BTC)_2$ for the conversion of **1** to **2,** a series of control experiments were performed using homogeneous catalysts such as $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$ and $ZrOCl_2.8H_2O$. The observed results are given in Table S3. The conversion of **1** to **2** was gradually increased with all these catalysts, but, high conversion of **1** is achieved with $Cu(NO_3)_2.3H_2O$ as a homogeneous catalyst which suggest that Cu^{2+} is the active site in promoting the conversion of **1** to **2**. Furthermore, comparing the selectivity of **2** between $Cu_3(BTC)_2$ and $Cu(NO_3)_2.3H_2O$ as catalyst suggest that the confined environment and the porous nature of $Cu_3(BTC)_2$ favors to achieve better selectivity of **2**. Also, these experiments indicate that the reaction takes place within the pores of $Cu_3(BTC)_2$ but however, one cannot avoid the reaction occurring on the surface of $Cu_3(BTC)_2$. In a way to understand whether Cu^{2+} in $Cu_3(BTC)_2$ acting as a Lewis acid site or redox centre, a control experiment was undertaken in the presence of pyridine as a catalyst poison. The observed results are given in entry 4, Table S3. The conversion of **1** catalyzed by $Cu_3(BTC)_2$ using TBHP as oxidant has no influence over the use of pyridine. If one assumes that Cu^{2+} in $Cu_3(BTC)_2$ is acting as a Lewis acid site, the conversion of **1** should have been reduced or completely suppressed under identical reaction conditions. Furthermore, the color of $Cu_3(BTC)_2$ was retained during the course of reaction and no color change is observed. These experimental data indicate that Cu^{2+} is behaving as a redox centre than a Lewis acid site when TBHP is used as oxidant.

Reusability experiments were performed for the oxidation of **1** to **2** using $Cu_3(BTC)_2$ as solid catalyst with TBHP as oxidant under the optimized reaction conditions. The conversion of **1** was 98%, 92%, 91% and 90% after 20 h for the fresh, first, second and third reuses respectively. These data indicate that the catalyst maintains its activity for three recycles without any decay in its activity. Furthermore, the catalyst stability was also investigated by comparing the fresh $Cu_3(BTC)_2$ with the recovered $Cu_3(BTC)_2$ for the conversion of **1** to **2** using TBHP as oxidant by different analytical and morphological studies. Analysis of the powder XRD patterns of the fresh $Cu_3(BTC)_2$ with the recovered $Cu_3(BTC)_2$ for the oxidation of **1** to **2** revealed that the structural integrity of $Cu_3(BTC)_2$ is maintained during the course of the reaction (Figure 3). This observation was also holds good for other substrates like diphenylsilane and triphenylsilane under identical conditions (Figure 3). Furthermore, comparison of FT-IR spectra of fresh $Cu_3(BTC)_2$ with the recovered $Cu_3(BTC)_2$ for the oxidation of **1** to **2** with TBHP as oxidant showed no significant changes in the stretching frequencies, thus indicating the retainment of the solid framework (Figure 4). On the other hand, SEM images of fresh and the recovered $Cu_3(BTC)_2$ for the reaction of **1** to **2** with TBHP indicate that the particle size is considerably reduced after the reaction.



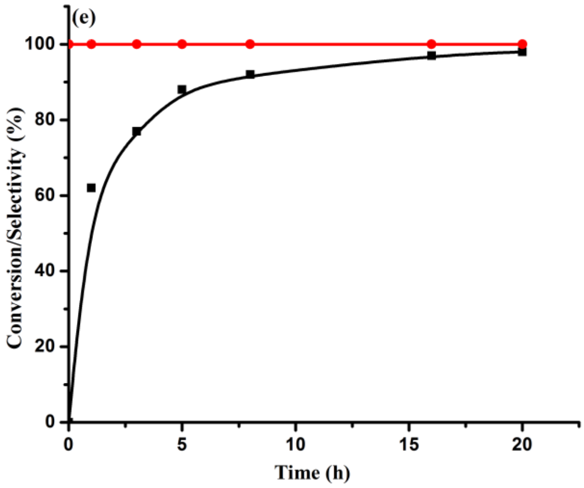


Figure 2. Conversion of **1** (black line) and selectivity of **2** (red line) using (a) $Cu_3(BTC)_2$, (b) Fe(BTC), (c) Zr(BDC)as MOF solid heterogeneous catalysts and (d) blank control experiment. Oxidation of triphenylsilane to the corresponding silanol using $Cu_3(BTC)_2$ as solid catalyst (e). Reaction conditions: **1** (1 mmol), TBHP (3 mmol), catalyst (25 mg), 60 ^{o}C.

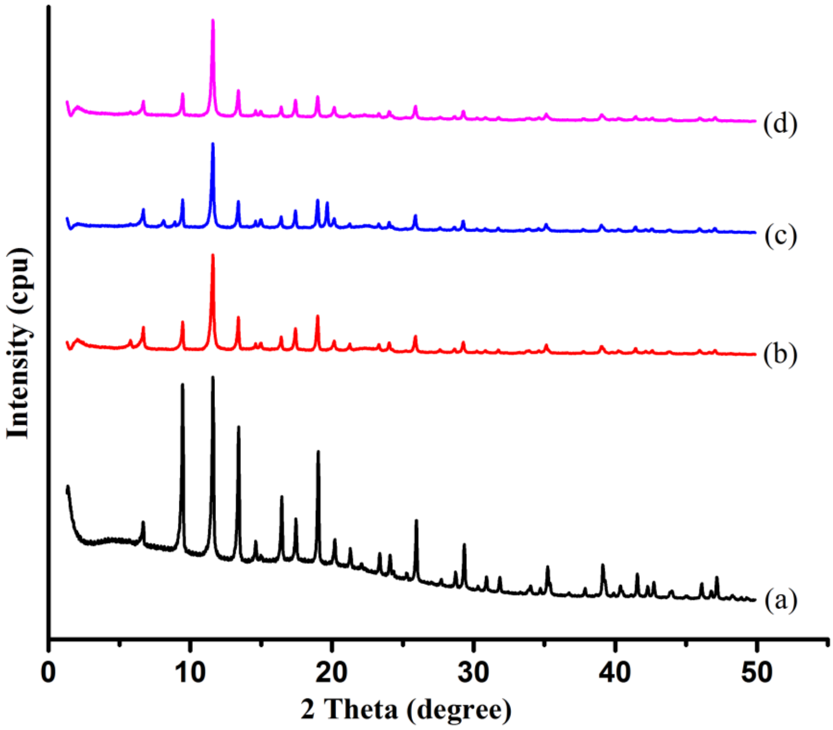


Figure 3. Powder XRD pattern of (a) fresh, (b) the recovered MOF after the reaction of **1** with TBHP, (c) the recovered MOF from triphenylsilane with TBHP and (d) the recovered catalyst from diphenylsilane with TBHP $Cu_3(BTC)_2$.

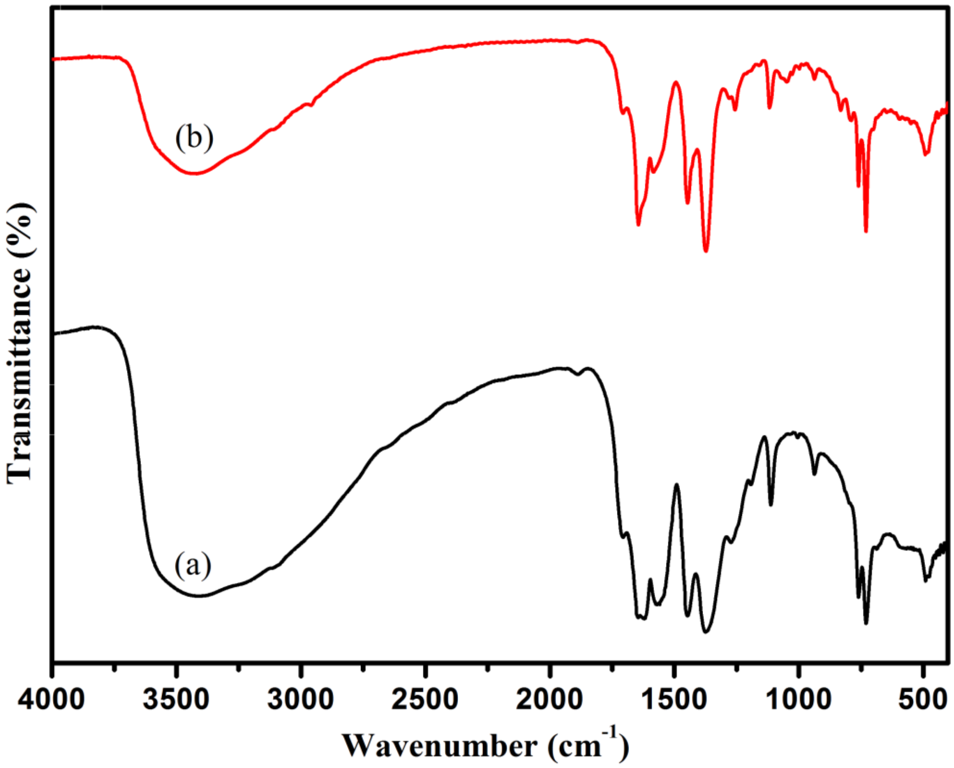


Figure 4. FT-IR spectrum of (a) fresh and (b) the recovered $Cu_3(BTC)_2$ after the reaction of **1** with TBHP.

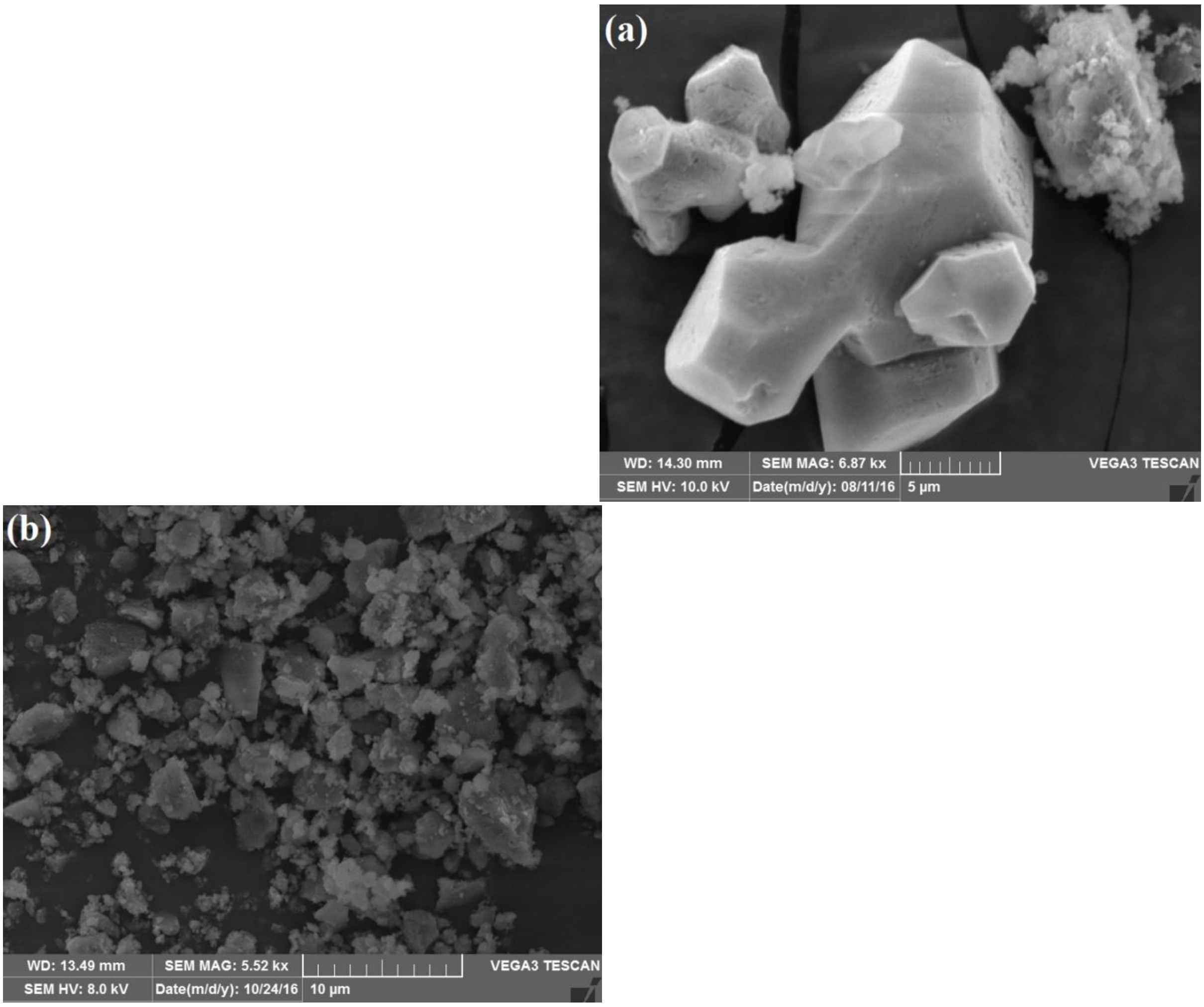


Figure 5. SEM images of (a) fresh and (b) the recovered $Cu_3(BTC)_2$ after the reaction of **1** with TBHP.

The scope of $Cu_3(BTC)_2$ was further studied with various silanes like diphenylsilane and triphenylsilane. The observed conversion and selectivity data are given in Table S4. The conversion of diphenylsilane to the corresponding silanol increased as a function of time but, however, the selectivity of silanol is 39% after 20 h. This may be due to the presence of two hydrogens and it is expected to give more than one silanol. This observation is in good agreement with earlier procedure showing higher reactivity of this substrate with $Cu_3(BTC)_2$ [49]. On the other hand, $Cu_3(BTC)_2$ promoted the oxidation of triphenylsilane to triphenylsilanol with 98% conversion and a complete selectivity of silanol under identical conditions (Figure 2).

3.3. Oxidation of silanes with water

In recent years, the use of MOFs as heterogeneous catalysts for various organic transformations has become a intensive research area. A highly challenging task in heterogeneous catalysis by MOFs is to develop catalytic systems involving MOFs as heterogeneous solid catalysts in the presence of water without compromising the stability under the experimental conditions. The chemical reactions using water as a medium has many advantages from environmental benignity, low cost, abundance, non-explosive, non-flammable and non-toxic. Recently, the catalytic transformation of silanes into silanols, using water as a green oxidant has been reported with many catalytic systems like nanoporous carbon [60], Au/SiO_2 [61], Au/KCC-1-APTS [62], Au/HAP [63], Au-MPBen [64], Ag-Hap [55], $[RuCl_2(p\text{-cymene})]_2$ [65], $[IrCl(C_8H_{12})]_2$ [66], $[Re(O)(hoz)_2(Solv)]B(C_6F_5)_4$ [67], Au NP decorated o-CNT [68], $[Re(O)(hoz)_2(CH_3CN)]B(C_6F_5)_4$ [69], $[RuCl_2(p\text{-cymene})]_2$/C [70] and $Ru_2(CO)_4(PPh_3)_2Br_2$ [71]. These reports triggered us to examine the activity of $Cu_3(BTC)_2$ for oxidation of silane to silanol using water as oxidant. The observed results are given in Table 1. Among a series of MOFs tested as catalysts for the conversion of **1** to **2** using water as an oxidant, $Cu_3(BTC)_2$ exhibited complete conversion of **1** with 99% selectivity of **2** (Table S5). On the other hand, Fe(BTC) and Zr(BDC) did not afford any conversion of **1** to **2** under identical reaction conditions. This observation is in accordance with earlier report in where $Cu_3(BTC)_2$ promotes dehydrogenative coupling between **1** and n-butanol [49]. Also, the blank control experiment in the absence of catalyst showed no oxidation of **1** to **2** under identical conditions. This observation was further supported by performing a series of control experiments with homogeneous catalysts like $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$ and $ZrOCl_2.8H_2O$. The observed results are given in Table S6. These data indicate that the conversion of **1** to **2** is effective only in the presence of $Cu(NO_3)_2.3H_2O$ while other homogeneous catalyst showed negligible conversions of **1**. These experiments clearly confirm that Cu^{2+} is essential to promote the conversion of **1** to **2** under the present experimental conditions. Further, comparing the product selectivity of **2** between $Cu(NO_3)_2.3H_2O$ and $Cu_3(BTC)_2$ indicates that the selectivity is always more than 98% in the presence of $Cu_3(BTC)_2$ and it is not influenced by the amount of water present in the reaction medium. In contrast, the selectivity of **2** decreased gradually from 72% at 30 min to 65% after 4 h, thus establishing the importance of the porosity of $Cu_3(BTC)_2$ to achieve very high selectivity. This can be considered as an indirect proof that the reaction takes place inside the pores of $Cu_3(BTC)_2$ but however, one cannot exclude the contribution from external active sites. On the other hand, another control experiment was performed using pyridine as a poison for the Lewis acid sites in $Cu_3(BTC)_2$. It was observed that the conversion of **1** was significantly reduced from 99% to 0% after 1 h in the presence of pyridine (Table S7, Figure 7). These experiment indicate that Cu^{2+} in $Cu_3(BTC)_2$ is acting as a Lewis acid site rather than redox centre. Furthermore, the color of $Cu_3(BTC)_2$ is changed from blue to pale brown by simultaneously liberating hydrogen gas. However, the color of $Cu_3(BTC)_2$ return back to its original color after 4 h. As it can be seen in Table 1, the conversion of **1** to **2** is very much influenced by the presence of water. A complete conversion of **1** was achieved after 1 h using $Cu_3(BTC)_2$ as catalyst either with 15 or 20 mmol of water with very high selectivity (~ 99%) of **2**. In contrast, the conversion of **1** was 98% after 4 h in the presence of $Cu_3(BTC)_2$ in THF without any water and the selectivity of **2** is 33% and this lower selectivity due to the formation of the corresponding disiloxane with 67%. These results clearly indicate the active role played by water as an oxidant/nucleophile under the present experimental conditions. Furthermore, the conversion of **1** and selectivity of **2** did not have any influence on catalyst loading. Under identical conditions, a complete conversion of diphenylsilane was observed with 76% selectivity of the corresponding silanol after 1 h (entry

2, Table S8). Further, the oxidation of diphenylsilane to the corresponding silanol showed 93% conversion with 76% selectivity at room temperature. On the other hand, efforts to convert triphenylsilane to triphenylsilanol was unsuccessful and this is in contrast with the data using TBHP as oxidant using $Cu_3(BTC)_2$ as catalyst (entry 4, Table S8). This result indicates that triphenylsilane encounter some steric hindrance to reach the Lewis acid site either at external/internal pores of $Cu_3(BTC)_2$. It is relevant to mention that the color of $Cu_3(BTC)_2$ is not changed during the course of the reaction.

Table 1. Oxidation of **1** into **2** using $Cu_3(BTC)_2$ as catalyst under various conditions.[a]

Entry	Water content (mmol)	Time (h)	Conversion of **1** (%)[b]	Selectivity of **2** (%)[b]
1	-	30 min	1	100
		1	30	100
		2	95	37(63)
		4	98	33(67)
2	5	30 min	3	100
		1	12	100
		2	45	100
		4	98	94
3	10	30 min	13	100
		1	91	98
		2	98	97
		4	100	96
4	15	30 min	96	99
		1	>99	99
		2	100	99
		4	100	99
5	20	30 min	97	99
		1	>99	99
		2	100	99
		4	100	99

[a]**Reaction conditions: 1** (1 mmol), H_2O, THF (1 mL), $Cu_3(BTC)_2$ (25 mg), 65 °C.

[b]Conversion and selectivity were determined by GC.

One of the issues to be addressed in heterogeneous catalysis is the stability of catalyst under the optimized reaction conditions. Hence, the stability of $Cu_3(BTC)_2$ was ascertained by reusing it in consecutive cycles, performing leaching experiment (hot filtration test) and analyzing the spent catalyst by powder XRD, SEM and FT-IR techniques. The catalyst was recovered from the reaction mixture after the required time, washed with ethyl acetate followed by acetonitrile and dried at 100 °C for 4 h. Then, this catalyst was reused in consecutive cycles with the fresh reactants under identical conditions. As it can be seen in Table S9, the catalyst was reused in four consecutive cycles without any decay in conversion of **1** (Figure 6). On the other hand, hot filtration test indicated the absence of copper in the reaction mixture, thus confirming the heterogeneity of the process under the present experimental conditions (Figure 7, Table S7). In addition, comparison of the chemical analysis data between fresh and three times reused $Cu_3(BTC)_2$ did not show any difference in the copper content, thus supporting the results of leaching experiment. Furthermore, comparison of the powder XRD patterns of fresh $Cu_3(BTC)_2$ with those recovered after the reaction with **1** and diphenylsilane indicated no noticeable changes in the crystalline nature of these samples, thus supporting the retainment of structural integrity of $Cu_3(BTC)_2$ using water as oxidant (Figure 8). In addition, comparison of the fresh $Cu_3(BTC)_2$ with the recovered after the reaction with **1** and four times reused $Cu_3(BTC)_2$ by FT-IR analysis showed no significant differences in the stretching frequencies (Figure 9). On the other hand, comparison of the structural morphology of fresh, the recovered catalyst after the reaction with **1** in water as oxidant and four times reused $Cu_3(BTC)_2$ by SEM show significant changes in their strutural morphology (Figure 10). It can be clearly seen that the crystallite size is reduced or surface is etched in the recovered as well as reused catalyst. This observation is in accordance with an earlier precedent in where $Cu_3(BTC)_2$ undergoes a structural deterioration over the exposure with water [72]. However, in any case, the activity of this catalyst is retained as evidenced from the reusability experiments. In addition, the catalyst stability was further ascertained by performing the reaction with 5 mmol under identical conditions. It was interesting to note that more than 99% conversion of **1** is achieved after 2 h with 99% selectivity of **2** (entry 5, Table S8). As the conversion and selectivity was almost quantitative, the reaction mixture was allowed to stir with ethylacetate and filtered. The removal of the solvent afforded 94% yield of **2**. As commented earlier, the conversion of **1** to **2** has been achieved with many catalytic systems involving the use of metal nanoparticles supported on different supports exhibiting high turnover numbers. However, this work reports the activity of $Cu_3(BTC)_2$ as a reusable heterogeneous MOFs catalyst for this reaction and the activity achiveved here is lower than with metal nanoparticles. All these data firmly support that $Cu_3(BTC)_2$ can be conveniently used as heterogeneous solid catalyst for the conversion of **1** to **2** using water as oxidant.

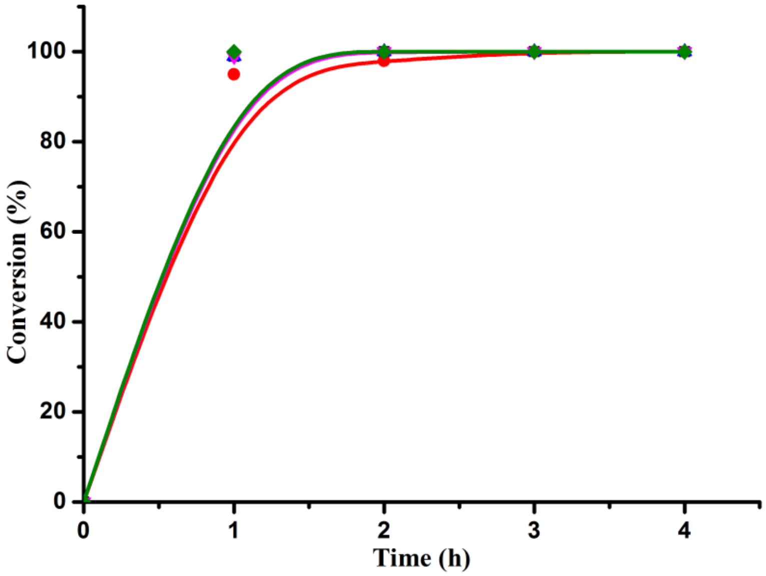


Figure 6. Reusability of $Cu_3(BTC)_2$ as heterogeneous solid catalyst for the oxidation of **1** to **2** using water as oxidant. Reaction conditions: **1** (1 mmol), H_2O (20 mmol), THF (1 mL) and $Cu_3(BTC)_2$ (25 mg), 65 °C, 4 h.

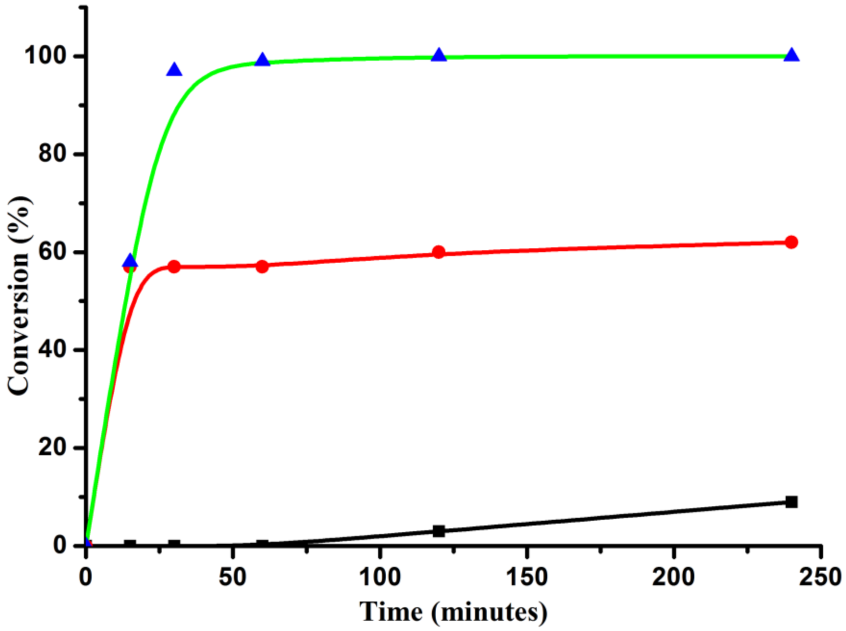


Figure 7. Leaching test for the oxidation of **1** to **2.** In the presence of catalyst (▲), the catalyst filtered after 15 minutes (●) and the poison test with pyridine under the optimized conditions (■).Reaction conditions: **1** (1 mmol), H_2O (20 mmol), THF (1 mL) and $Cu_3(BTC)_2$ (25 mg), 65 °C, 4 h.

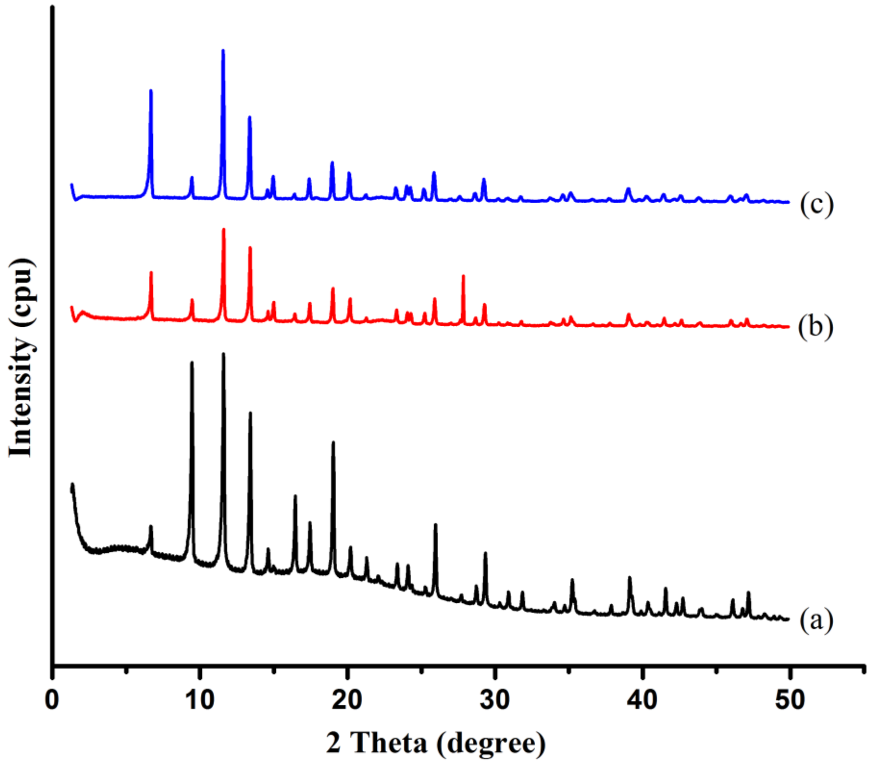


Figure 8. Powder XRD pattern of $Cu_3(BTC)_2$ (a) fresh, (b) recovered after the reaction of **1** with H_2O, (c) recovered after the reaction of diphenylsilane with H_2O.

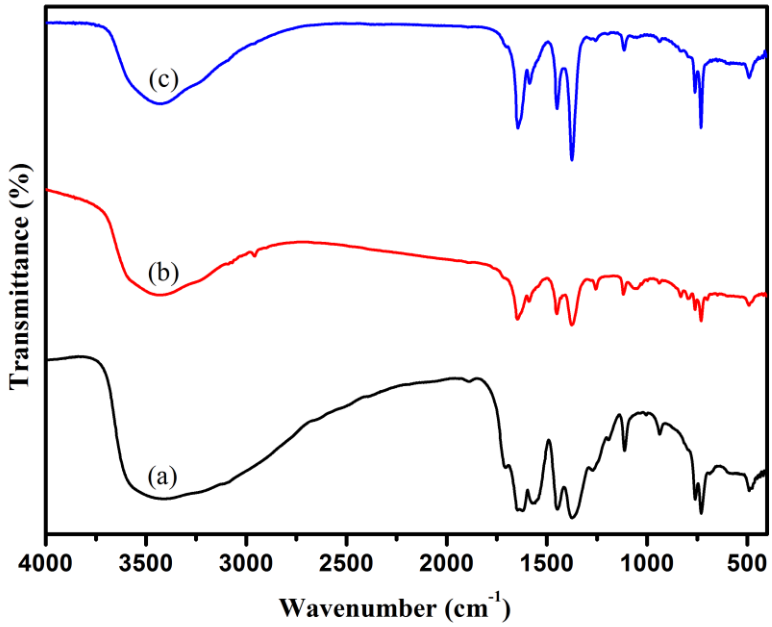


Figure 9. FTIR spectrum of (a) fresh, (b) recovered after the reaction from **1** and (c) four times used $Cu_3(BTC)_2$.

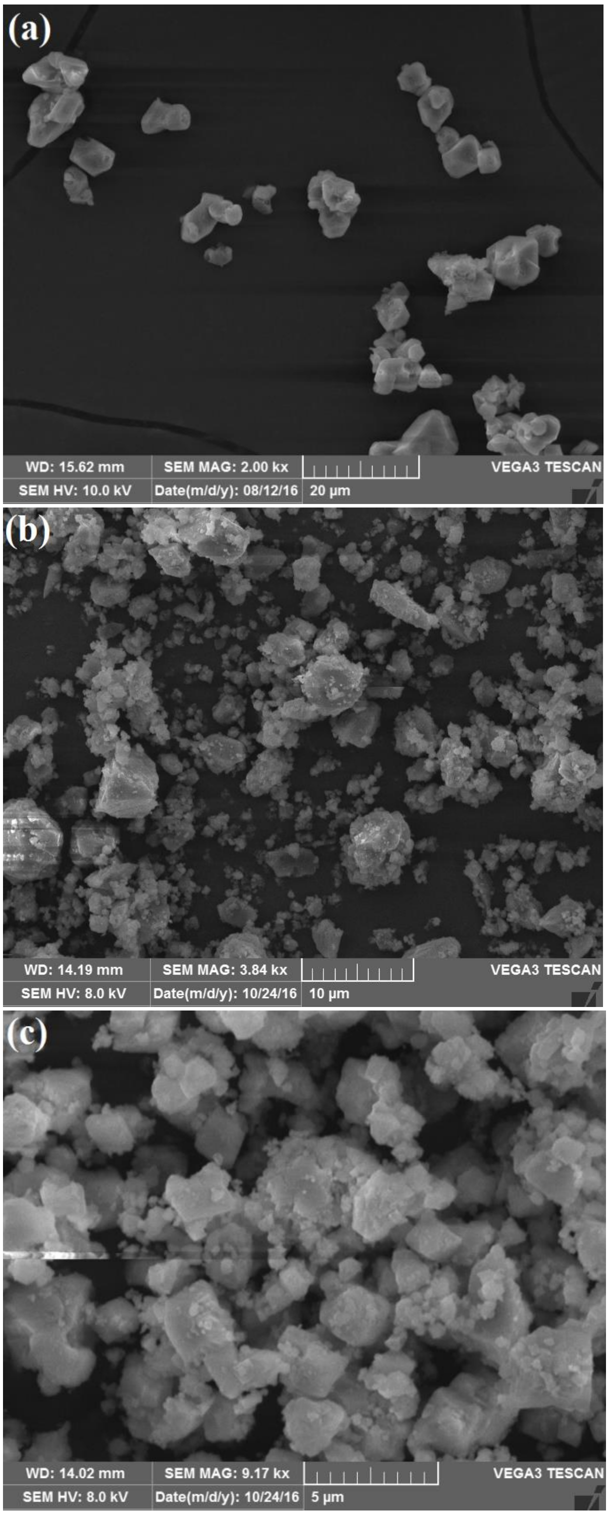
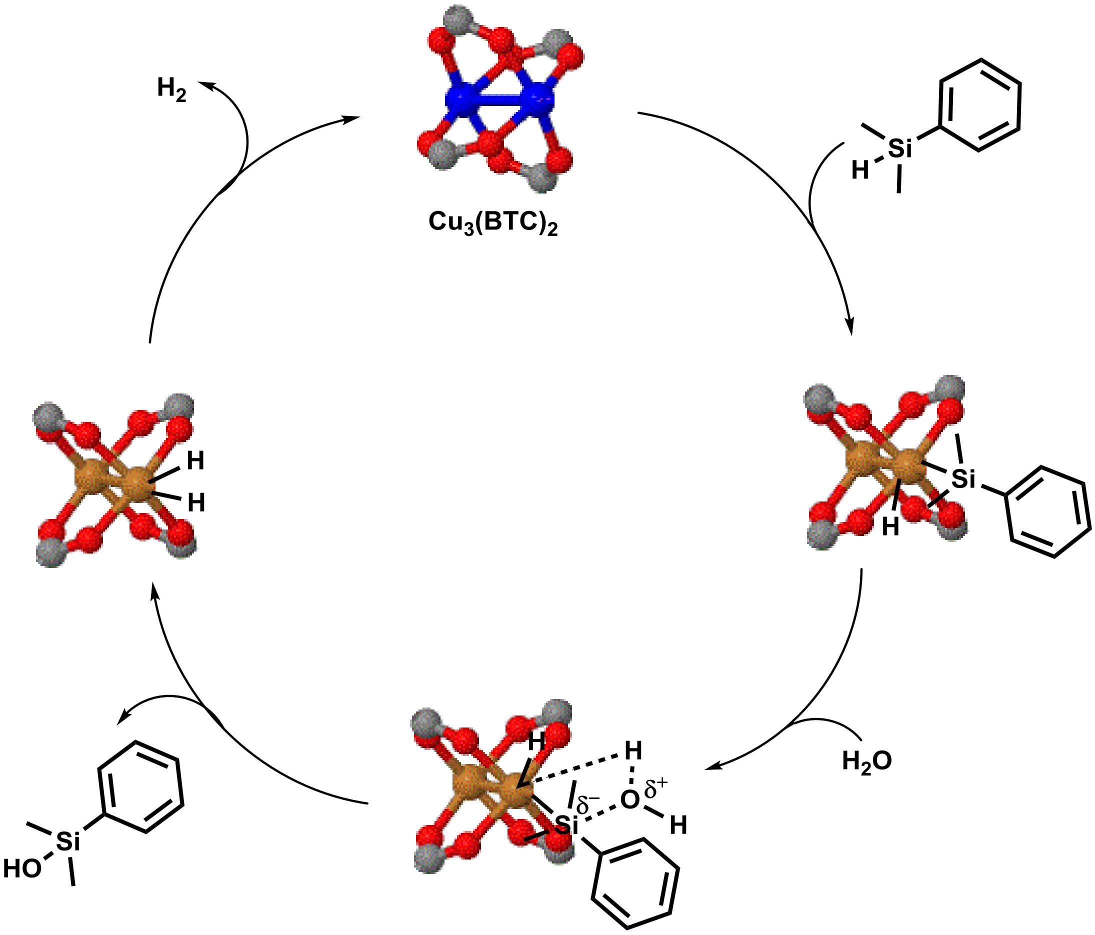


Figure 10. SEM images of (a) fresh, (b) recovered after the reaction of **1** in water and (c) four times used $Cu_3(BTC)_2$.

3.4. Proposed mechanism

Based on our findings, we propose a tentative mechanism for the oxidation of **1** to **2** using $Cu_3(BTC)_2$ using water as an oxidant. $Cu_3(BTC)_2$ interacts with **1** by changing its blue color to pale brown as shown in Scheme 2. Then, water reacts with **1** to form an intermediate which later gives the desired product **2**. It is experimentally observed that the liberation of hydrogen stops at lower reaction time (15 min). Further, the liberation of hydrogen from this reaction is confirmed by gas chromatography. In addition, the color of $Cu_3(BTC)_2$ slowly returns back to its original color.



Scheme 2. A proposed mechanism for the oxidation of **1** to **2** with water using $Cu_3(BTC)_2$ as heterogeneous solid catalyst.

4. Conclusions

A series of MOFs were examined for the conversion of **1** to **2** either in the presence of TBHP or with water as oxidants. It was noticed that $Cu_3(BTC)_2$ shows superior activity but however Fe(BTC) and Zr(BDC) did not show any activity with H_2O as oxidant. On the other hand, quantitative conversion of **1** was achieved using water as an oxidant in the presence of

$Cu_3(BTC)_2$ as a catalyst with very high selectivity to **2**. The catalyst stability was studied by powder XRD, FT-IR and SEM using TBHP and water as oxidants and observing no structural changes were observed under the present experimental conditions. However, SEM images of the fresh and reused $Cu_3(BTC)_2$ showed a considerable change in their crystallite size both in TBHP and H_2O as oxidants. Finally, hot filtration test showed the absence of Cu^{2+} in the solution under the present experimental conditions, thus, further confirming the stability of $Cu_3(BTC)_2$ and heterogeneity of the process. A series of control experiments indicate that Cu^{2+} is essential to convert **1** to **2** under the present experimental conditions. Further, Cu^{2+} in $Cu_3(BTC)_2$ acts as redox centre while the use of TBHP whereas it behaves as a Lewis acid using water as oxidant.

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List of Captions

Scheme Captions

Scheme 1. Oxidation of silane into silanol using TBHP or water as oxidant in the presence of MOFs as heterogeneous solid catalysts.

Table Caption

Table 1. Oxidation of **1** into **2** using $Cu_3(BTC)_2$ as catalyst under various conditions. [a]

Figure Captions

Figure 1. Time conversion plot for the conversion of **1** using $Cu_3(BTC)_2$ as heterogeneous solid catalyst with (a) 1, (b) 2 and (c) 3 mmol of TBHP as oxidant. Reaction conditions: **1** (1 mmol), TBHP (mmol), $Cu_3(BTC)_2$ (25 mg), 60 ^oC.

Figure 2. Conversion of **1** (black line) and selectivity of **2** (red line) using (a) $Cu_3(BTC)_2$, (b) Fe(BTC), (c) Zr(BDC)as MOF solid heterogeneous catalysts and (d) blank control experiment. Oxidation of triphenylsilane to the corresponding silanol using $Cu_3(BTC)_2$ as solid catalyst (e). Reaction conditions: **1** (1 mmol), TBHP (3 mmol), catalyst (25 mg), 60 ^oC.

Figure 3. Powder XRD pattern of (a) fresh, (b) the recovered MOF after the reaction of **1** with TBHP, (c) the recovered MOF from triphenylsilane with TBHP and (d) the recovered catalyst from diphenylsilane with TBHP $Cu_3(BTC)_2$.

Figure 4. FT-IR spectrum of (a) fresh and (b) the recovered $Cu_3(BTC)_2$ after the reaction of **1** with TBHP.

Figure 5. SEM images of (a) fresh and (b) the recovered $Cu_3(BTC)_2$ after the reaction of **1** with TBHP.

Figure 6. Reusability of $Cu_3(BTC)_2$ as heterogeneous solid catalyst for the oxidation of **1** to **2** using water as oxidant. Reaction conditions: **1** (1 mmol), H_2O (20 mmol), THF (1 mL) and $Cu_3(BTC)_2$ (25 mg), 65 ^oC, 4 h.

Figure 7. Leaching test for the oxidation of **1** to **2.** In the presence of catalyst (▲), the catalyst filtered after 15 minutes (●) and the poison test with pyridine under the optimized conditions (■).Reaction conditions: **1** (1 mmol), H_2O (20 mmol), THF (1 mL) and $Cu_3(BTC)_2$ (25 mg), 65 ^oC, 4 h.

Figure 8. Powder XRD pattern of $Cu_3(BTC)_2$ (a) fresh, (b) recovered after the reaction of **1** with H_2O, (c) recovered after the reaction of diphenylsilane with H_2O.

Figure 9. FTIR spectrum of (a) fresh, (b) recovered after the reaction from **1** and (c) four times used $Cu_3(BTC)_2$.

Figure 10. SEM images of (a) fresh, (b) recovered after the reaction of **1** in water and (c) four times used $Cu_3(BTC)_2$.

Scheme 2. A proposed mechanism for the oxidation of **1** to **2** with water using $Cu_3(BTC)_2$ as heterogeneous solid catalyst.