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ARTICLE TYPE

## Tetrabutylammonium tribromide impregnated MCM-48 as a heterogeneous catalyst for selective oxidation of sulfides

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We report here tetrabutylammonium tribromide supported on MCM-48 as a highly efficient heterogeneous catalyst for the selective oxidation of sulfides, in ethanolic medium using hydrogen peroxide as an oxidant. The aforementioned oxidation reactions were found to proceed rapidly (20 min) and in good yield (85–99%) (17 examples). The oxidation products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. The catalytic property was analysed by TEM, XRD and BET-surface area measurement. No over-oxidation of the substrates was observed (analysed by GC), and the catalyst was effectively recycled for five consecutive cycles without any significant loss in its catalytic activity.

TBATB (tetrabutylammonium tribromide) is widely used as a brominating agent.<sup>1–3</sup> Recently, organic tribromide have been used for oxidations of some selected organic substrates.<sup>4–5</sup> Among the various catalytic processes, TBATB has drawn the attention of researchers because of its stability, cheapest catalyst, easier methods of preparation and has certain advantages over molecular bromine.<sup>6</sup> In 1865, Maercker and co-worker first reported the transformation of sulfide to sulfoxide.<sup>6–7</sup> In 2003 Matteucci *et al.* reported Sc(OTf)<sub>3</sub> mediated highly selective oxidation of sulfides, where no catalyst recovery was possible, which is the drawback of this method.<sup>8</sup> In 2011 Maggi *et al.* reported metal free oxidation of sulfides, where sulfones remained as a byproduct.<sup>9</sup> Unfortunately, most of the methods used have certain limitations such as hazardous, toxic reagents and metal toxicity accompanied by over oxidation to the sulfone and high price of catalysts.<sup>10–14</sup> Moreover, a challenge in this reaction could be the complete selectivity for sulfoxide products. Although some homogeneous tribromide has been found to be

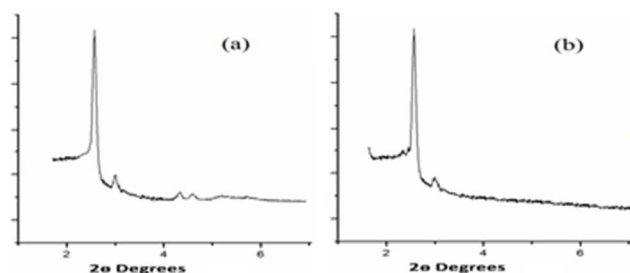
effective for oxidation of sulfides, still they have certain limitations.<sup>15</sup> In homogeneous condition, catalyst recovery becomes difficult and this results a bad impact on the commercial productivity.<sup>16</sup>

In 2005, D.H. Koo *et al.* reported WO<sub>3</sub> particles supported on MCM-48 work as a highly efficient and selective heterogeneous catalyst for the oxidation of olefins, sulfides, and cyclic ketones using hydrogen peroxide or peracetic acid.<sup>17</sup> In 2013, Rostami *et al.* reported MNPs-DABCO tribromide (Magnetic nanoparticle-supported the 1,4-diazabicyclo [2.2.2] octane tribromide) catalyst for the chemoselective oxidation of sulfide using H<sub>2</sub>O<sub>2</sub> under solvent-free conditions.<sup>18</sup>

In this current work we have developed metal free TBATB immobilized on MCM-48 heterogenous system for oxidation of sulfides using H<sub>2</sub>O<sub>2</sub> as an oxidant, since hydrogen peroxide is widely accepted as a green and effective oxidant in organic oxidations.<sup>19–20</sup>

MCM-48 (Mobile composite of matter), mesoporous materials, have attracted considerable attention due to their high surface areas and large pore sizes.<sup>21</sup> However, owing to its poor hydrothermal stability and weak acidity, direct catalytic application of pure silica MCM-48 is limited.<sup>22</sup> In order to overcome these drawbacks, four immobilization strategies were involved.<sup>23</sup> Among these post-grafting (post-synthesis) and co-condensation (direct-synthesis) are the two main methods for the construction of mesoporous silica-supported based catalysts. These immobilization strategies worked out well with various mesoporous silica-supported transition-metal-based catalysts. Limitations to transition-metal functionalities may be incorporated into the pore-wall network, which incurs some loss of functionality. In addition, involvement of high temperature

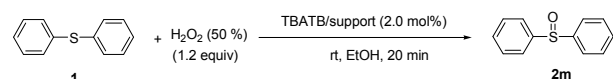
environment, mesoporous channels sometime decrease the pore size, which may reduce catalytic efficiency.<sup>24</sup> Herein, we report metal and surfactant free direct synthesis of TBATB-MCM-48 catalyst. In typical procedure, TBATB (160 mg, 0.5 mmol),  
 5 MCM-48 (1.0 g), and DCM (20 mL) were placed in a 50 mL two-neck flask with a magnetic stirring bar. The reaction mixture



**Fig. 1** Low angle XRD patterns of (a) pure silica MCM-48, and (b)

impregnation (TBATB/MCM-48)

**Table 1** Effect of supporting materials on sulfide oxidation<sup>a</sup>



Entry	Supporting materials	conv <sup>b</sup>	selec(% <sup>c</sup> )	
			sulfoxide	sulfone
1	-	30	70	23
2	SiO <sub>2</sub>	48	90	8
3	alumina	57	56	39
4	MCM-41	87	90	9
5	MCM-48	100	99	negligible
6	MCM-48 <sup>d</sup>	100	26	70
7	MCM-48 <sup>e</sup>	65	95	4
7	MCM-48 <sup>f</sup>	100	99	negligible
8	MCM-48 <sup>g</sup>	100	81	18

<sup>a</sup>substrate **1** (0.5 mmol), 1.2 equiv of H<sub>2</sub>O<sub>2</sub>, TBATB/support (2.0 mol%) in  
 15 EtOH (2 mL), <sup>b</sup>cConversion and selectivity were determined by GC using toluene as internal standard. <sup>c</sup>Condition: 3.0 equiv of H<sub>2</sub>O<sub>2</sub>. <sup>d</sup>Condition: TBATB/MCM-48 (1 mol%), <sup>e</sup>Condition: TBATB/MCM-48 (3 mol%), <sup>f</sup>Condition: 2h, 80 °C

being stirring for 72 h at 0 °C under an argon atmosphere. The solution was filtered and washed with DCM, and the obtained solid was dried in vacuo. The observed catalyst was characterized by X-ray diffraction (XRD) (Fig.1) and Tunneling electron microscopy (TEM) analysis (ESI).

25 In our initial attempts, we choose diphenylsulfide as model substrate. For TBATB/MCM-48 catalyst, we obtained 100% conversion of diphenylsulfide and product selectivity for sulfoxide was 99% (Table1, entry 5). Thus, TBATB/MCM-48 acted as an excellent catalyst for the selective oxidation of  
 30 diphenylsulfide to sulfoxide. It is worth noting that TBATB can somewhat catalyze the reaction but only at a conversion of 30% in 20 minutes (selectivity for sulfoxide and sulfone at 70% and 23%, respectively). Therefore, supporting materials are essential for the catalytic reaction in given desired time.

**Table 2** Substrate scope<sup>a</sup>( yield <sup>b</sup>)


<sup>a</sup> Reaction conditions: substrate **1** (0.5 mmol), TBATB/MCM-48 (2 mol%), 1.2 equiv H<sub>2</sub>O<sub>2</sub>, ethanol (2 mL), 20 min. <sup>b</sup>Yields were determined  
 40 by GC using toluene as the internal standard.

We further investigated the catalytic efficiency by varying the amount of the supporting materials with the other conditions kept the same as above. As shown in Table 1, the catalyst is indeed remarkably efficient: even a minimal amount (1 mol%) of TBATB/MCM-48 catalyst gave rise to 65% conversion (Table 1, entry 7). When the catalyst amount was between 2 mol% and 3 mol%, the conversion of sulfide and the selectivity for sulfoxide did not change appreciably; thus, we chose 2 mol% catalyst for all of the experiments hereafter. With respect to the effect of reaction temperature on the product selectivity, we found that at high temperatures (Table 1, entry 8, e.g. 80 °C) over-oxidation of the sulfoxide product to sulfone occurs, which reduces the selectivity for the target product.

With the optimum conditions established (Table 1, entry 5), we explored the scope to study the oxidation of other sulfides (Table 2). The other substrates, aliphatic and aromatic sulfides, could be oxidized to the corresponding sulfoxides. All the reactions occurred with complete selectivity for sulfoxide formation, no overoxidation products such as sulfones were detected in the reaction mixtures. The reactivity and conversion were dependent on the nature of the substituent. In the case of benzylic sulfides no oxidation was observed at the benzylic C–H bond. Similarly, allyl sulfides and aryl allyl sulfides could be oxidized to the corresponding sulfoxides without affecting the carbon–carbon double bond. Aryl/Benzyl sulfides were providing excellent yield of sulfoxides while diallyl and dialkylsulfides were moderately reactive providing the corresponding sulfoxides.

The efficiency of a heterogeneous catalyst is evaluated in terms of its recyclability and stability. The catalyst TBATB/MCM-48 system was quantitatively recovered by a simple centrifugation after the reactions and was readily reused in the next runs without losing its catalytic activity. A plot of isolated yield (%) of catalyst vs. number of cycles (5 cycles) is shown in Fig. 2. The TEM images of the fresh and recovered catalyst after the 5<sup>th</sup> cycle show that the morphology of the catalyst remained unaltered (ESI).

The N<sub>2</sub> adsorption-desorption isotherms of MCM-48 and TBATB-MCM-48 (fresh and spent) samples are shown in Fig. 3. It is shown that all three isotherms have the typical

characteristics of the mesoporous material isotherms and are of the type IV according to the IUPAC classification. The surface areas and pore sizes of MCM-48, TBATB/MCM-48-fresh and TBATB/MCM-48-spent samples were 1308.3, 1005.6, and 1005.9 m<sup>2</sup>/g and 2.17, 2.43, and 2.42 nm, respectively.

Although, the exact mechanism of this reaction is not clear at this stage, it probably involves the in situ generation of bromine from TBATB-MCM-48 system (Scheme1). Based on the previous studies,<sup>25</sup> the generated bromine involves in oxidation process and completes the catalytic cycle.

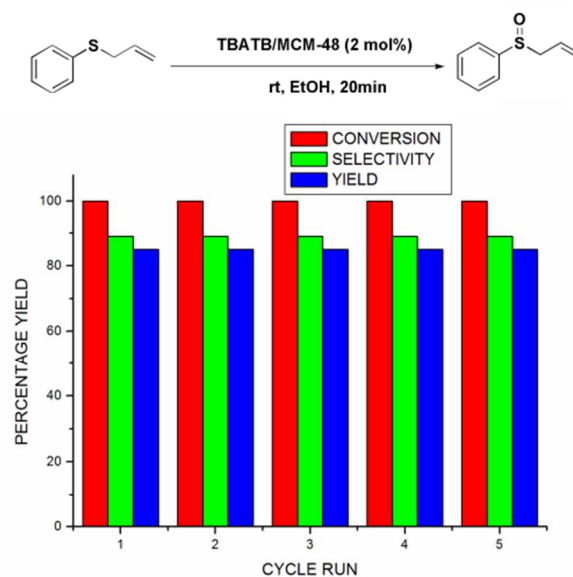


Fig. 2 Recyclability of catalyst

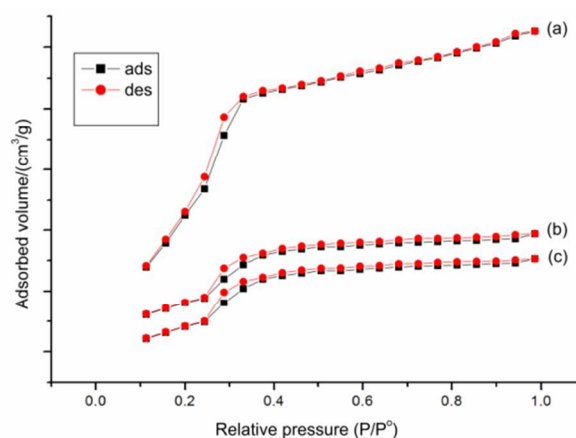
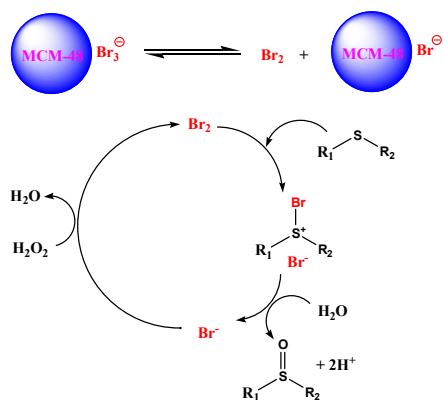


Fig. 3 N<sub>2</sub> adsorption-desorption isotherms of (a) MCM-48 (b) fresh TBATB-MCM-48, and (c) spent TBATB-MCM



**Scheme 1** Plausible mechanism

In summary, we have shown that TBATB-MCM-48 work as a highly efficient and selective heterogeneous catalyst for the oxidation of sulfides. The catalyst can be reused several times without any activity loss. The proposed method is also advantageous from the standpoint of metal free condition and operational simplicity; furthermore, it can be applicable to large-scale reactions.

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