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Short Communication

Novel mesoporous polyoxometalate hybrid catalysts for heterogeneous oxidation of thioethers

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ABSTRACT

$K_6P_2W_{18}O_{62}$ and $K_{14}[NaP_5W_{30}O_{110}]$ polyoxometalate salts are synthesized and immobilized within MCM-48, SBA-3, SBA-15 and NH_3^+ functionalized mesoporous silicas. The newly designed hybrid materials are studied as catalysts for oxidation of thioethers. Preyssler complex is found to be a more active catalyst compared to its Dawson analog. Texture and chemical composition of the silica framework is shown to have indispensable effect on oxidation efficiency, stability, and reusability of catalysts. Catalysts with larger pores are proved to be more proper for the oxidation of relatively large thioethers and functionalization improves catalyst's properties.

1. Introduction

Heterogeneous oxidation of sulfides has received much attention as one of the promising methods for both sulfur detoxification and production of sulfoxides [1]. Sulfoxides are important intermediates for synthesis of many interesting chemically and biologically active compounds [2–6]. Many papers and patents concerning oxidation of sulfides have been published and among these, polyoxometalate catalytic systems have received special attention as efficient environmental friendly catalytic systems [7–9].

Polyoxometalates (POMs) are an immense class of metal-oxo anionic clusters of mainly tungsten and molybdenum which are known to be active green catalysts for thioether oxidation. Dozens of structural types of polyoxometalates are known to date [10]. Among these, Keggin POMs are the most studied catalysts [11–14] while few studies are concerned about other structures such as Wells–Dawson and Preyssler [15,16]. Wells–Dawson anions are ellipsoidal structures of POMs with general formula of $PM_{18}O_{68}$, consisting of two lacunary Keggin species (with D_{3h} symmetry) linked directly across the lacunae. Each of the PM_9O_{34} lacunary fragments are formed by removal of three MO_3 groups from three adjacent M_3O_{13} subunits in the parent Keggin structure (Fig. 1a) [10]. Preyssler anions appear as ellipsoids (prolate spheroids) built of five PM_6 units arranged in a crown so that the whole anion has an internal fivefold symmetry axis (Fig. 1b). Perpendicular to this axis is a mirror plane containing the five P atoms and metal atoms are distributed in four parallel planes perpendicular to the axis [17].

Despite the advantages, there exist some drawbacks about catalysis with POM based systems: relatively low thermal stability, high solubility in polar solvents producing separation problems, and low surface area which is an important restriction for catalytic systems. All these limitations may be satisfied by grafting POMs within proper heterogenizing supports, which is a great step to extending catalytic applications of POM based catalysts [18,19]. A new paradigm in heterogeneous POM catalysis is made possible by their fine dispersion within the uniform and tailored pores and channels of MCM-type [20,21] and SBA-type [22,23] mesoporous silicas. In addition to these merits, more intriguing hybrid catalytic systems may be contrived by rational design and tailoring of hydrophobicity, adsorption characteristics and reactivity of the immobilizing supports through their modification with organic functional groups [24,25]. Functional groups enhance the interactions of guest molecules with the support material either by physical forces (i.e. hydrogen bonding and electrostatic interactions) or chemical bonding and allow higher and more stable loading [26–28].

In our previous work, we studied effect of mesoporous silica support on oxidation activity of heterogeneous Keggin heteropoly acid systems [22]. Here, we would like to make an extension to larger Preyssler and Dawson POMs and study the support's textural and chemical effect on their catalytic activity. The newly designed hybrid systems will be applied to oxidize thioethers and their catalytic efficiency will be truly studied and compared. The systems are also tested to demonstrate heterogeneous nature and reusability.

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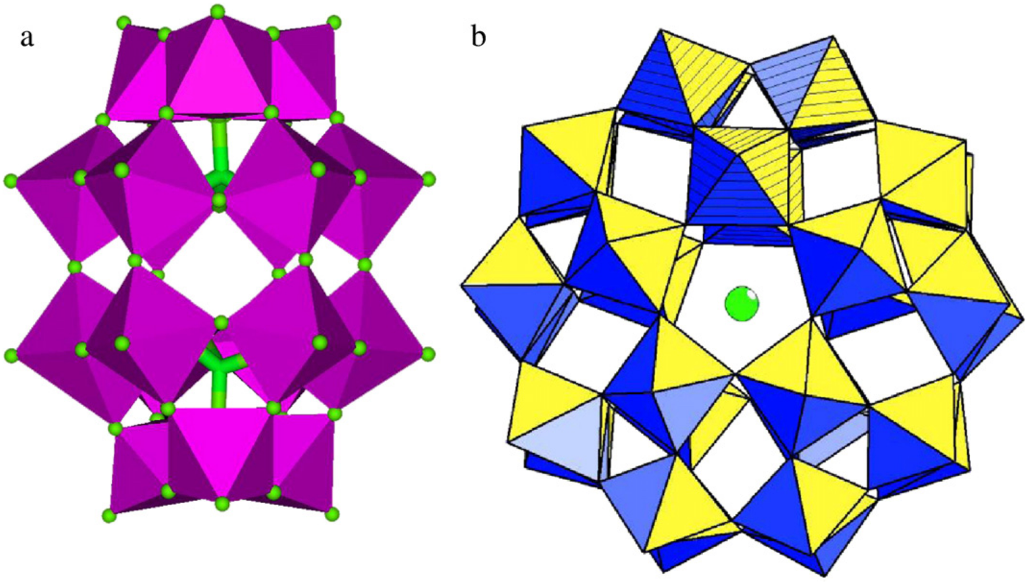


Fig. 1. Structure of (a) Wells–Dawson $[P_2W_{18}O_{62}]^{6-}$ and (b) Preyssler $[NaP_5W_{30}O_{110}]^{14-}$ polyoxometalate anions (the atom in the middle of Preyssler structure represents sodium).

2. Experimental

2.1. Synthesis of POMs

Synthesis of $K_6P_2W_{18}O_{62} \cdot 10\ H_2O$ (labeled as P_2) Wells–Dawson salt is conducted according to the literature [29]. To produce the $K_{14}[NaP_5W_{30}O_{110}]$ (labeled as P_5) Preyssler salt, 26.5 ml aqueous solution of phosphoric acid is added to 30 ml aqueous solution Na_2WO_4–$2H_2O$ (33 g). The mixture is then transferred to a Teflon line and further reacted at 120 °C for 18 h. Then, 30 ml 4.5 M solution of KCl is added into the resulting mixture to give white precipitate. The product is filtered and washed with 2 M aqueous solution of CH_3COOK and methanol. The potassium salt is recrystallized twice to obtain pure $K_{14}[NaP_5W_{30}O_{110}]$ [17].

2.2. Synthesis of mesoporous silicas

Synthesis of SBA-15 is conducted according to the literature [30]. Pluronic P123 is used as a template, and the silica source is tetraethylorthosilicate (TEOS). The molar ratio of the reaction mixture is 1 TEOS: 0.0168 P123: 5.8 HCl: 155 H_2O.

Functionalization of the as synthesized SBA-15 mesoporous silica with pr-NH_3^+ (i.e. —CH_2—CH_2—CH_2—NH_3^+) group is carried out in two steps according to our previously reported method [26].

Cetyltrimethylammonium bromide (CTAB) and TEOS are used as surfactant and silica source, respectively, to synthesize SBA-3 [31]. The molar composition of the reaction mixture is 0.12 CTAB: 1 TEOS: 9 HCl: 162 H_2O.

Synthesis of MCM-48 is carried out according to literature [32] using the following molar composition: 1.0 TEOS: 0.65 CTAB: 0.5 KOH: 62 H_2O.

All the as synthesized mesoporous materials are calcined at 600 °C in air for 6 h.

2.3. Preparation of mesoporous hybrid catalysts

0.5 g POM is dissolved in 10 ml acetonitrile and ethanol 1:1 mixture and 0.5 g of mesoporous silica (SBA-15, SBA/NH_3^+, SBA-3, or MCM-48) is then suspended in the resulting solution. After 24 h of stirring at 70 °C, the solid product is centrifuged and washed several times with ethanol to eliminate any unstably immobilized species. The resulting heterogeneous systems are then labeled as SBA-15/P_2, SBA-15/P_5, [SBA/NH_3^+]/P_5, SBA-3/P_5, MCM-48/P_5.

2.4. Characterization of the samples

Characterization of the synthesized organic–inorganic hybrid mesoporous catalysts is performed by different conventional techniques. X-ray powder diffraction (XRD) data are acquired on a Philips X-Pert diffractometer using Cu K_α radiation (40 kV, 30 mA, with time step of 1°/s). The carbon, nitrogen and hydrogen analyses are carried out using Perkin-Elmer 2004(II) CHN analyzer. Surface area and porosity are measured on NOVA 2200E Quantachrome instrument and results are analyzed via Barrett–Joyner–Halenda (BJH) method. Atomic absorption data are acquired by contrAA 700 using flame technique.

2.5. Oxidation reaction

The newly designed hybrid catalysts are studied for oxidation of thioethers. Catalytic oxidation reactions are performed at room temperature and atmospheric pressure in a round bottom flask under magnetic stirring. 1 mmol of thioether substrate is oxidized in presence of 30% H_2O_2 (1.8 mmol) as oxidant, 0.9 ml of dichloromethane as solvent, and 50 mg of the newly designed mesostructured catalysts. Regarding the POM content in each of the systems (Table 1), the amount of POM species present in the reaction mixture could be estimated as 0.16, 0.8, 1.4, 0.6, and 0.9 μmol for SBA-15/P_2, SBA-15/P_5,

Table 1
Structural properties and chemical composition of mesostructured hybrid catalysts.

Sample	d spacing (nm)	Unit cell parameter (nm)	POM content (wt.%)
SBA-15	7.95	9.2[a]	–
SBA-15/P_2	7.5	8.6[a]	14.3
SBA-15/P_5	7.2	8.4[a]	12.8
SBA-15/NH_3^+	7.8	8.9[a]	–
[SBA-15/NH_3^+]/P_5	7.3	8.5[a]	21.9
SBA-3	3.1	3.6[a]	–
SBA-3/P_5	2.9	3.3[a]	8.7
MCM-48	3.3	8[b]	–
MCM-48/P_5	3.1	7.5[b]	14.5

[a] $a_0 = 2d_{100}/\sqrt{3}$.
[b] $a_0 = d_{211}/\sqrt{6}$.

$[SBA/NH_3^+]/P_5$, $SBA\text{-}3/P_5$, and $MCM\text{-}48/P_5$ catalysts, respectively. Catalytic reactions are monitored using gas chromatography, GC, HP5890 chromatograph with capillary column and n-dodecane (0.1 mmol) is used as internal standard for product quantification.

3. Results and discussion

3.1. Characterization of catalysts

Low angle powder X-ray diffraction (XRD) patterns of pure, functionalized, and POM containing mesoporous materials are depicted in Fig. 2. The three distinct Bragg diffractions, (100), (110), and (200), are characteristics of a highly ordered two-dimensional hexagonal mesoscopic structure of pure SBA-15, SBA/NH_3^+ and SBA-3. As for MCM-48, the well resolved (211), (400), (420), and (322) diffractions are indicative of 3D cubic structure with Ia3d space group [33]. Presence of the reflections in all diffractograms confirms the pore structural maintenance upon functionalization and incorporation of guest molecules. Intensity and resolution of reflections is based solely on the degree of ordering in the material's pore array and arises from the electron density gradient between the walls and pores. Incorporation of POM guests reduces the order of the mesostructured system and leads to increased phase cancelation between X-rays scattered from the walls and pores. Thus, a decrease in the intensity of the Bragg reflections in the low angle region is evidenced [34]. In order to understand NH_3^+ content in the functionalized support, CHN elemental analysis is conducted. Results are indicative of 1.98% of N, 5.12% of C in the SBA/NH_3^+ mesoporous material.

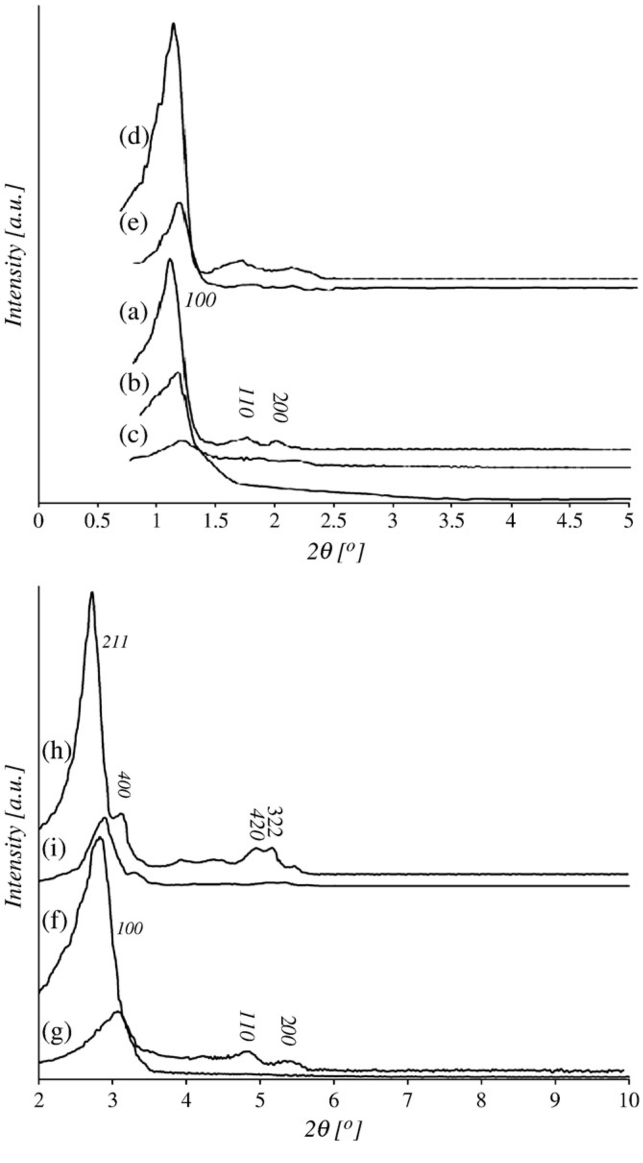


Fig. 2. Low-angle XRD patterns of (a) SBA-15, (b) $SBA\text{-}15/P_2$, (c) $SBA\text{-}15/P_5$, (d) SBA/NH_3^+, (e) $[SBA/NH_3^+]/P_5$, (f) SBA-3, (g) $SBA\text{-}3/P_5$, (h) MCM-48, (i) $MCM\text{-}48/P_5$.

Table 2
Textural parameters of the hybrid catalysts and mesoporous supports (pore diameter and total pore volume are calculated based on the desorption branch).

Sample	S_{BET} (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)
SBA-15	656	6.2	0.75
$SBA\text{-}15/NH_3^+$	384	4.7	0.61
SBA-3	1435	2.2	0.96
MCM-48	1055	3.2	1.3
$SBA\text{-}15/P_2$	538	5.6	0.64
$SBA\text{-}15/P_5$	449	4.6	0.52
$[SBA\text{-}15/NH_3^+]/P_5$	269	4.1	0.48
$SBA\text{-}3/P_5$	473.2	0.8	0.39
$MCM\text{-}48/P_5$	561	1.03	0.43

The structural and physicochemical parameters of the newly designed catalysts are summarized in Table 1. The d-spacing (calculated from Bragg equation) and unit cell parameters of the designed materials are determined based on the low-angle XRD patterns, surface area is estimated based on BET analysis, and pore diameters and pore volume are obtained using BJH theory [35] (Table 2). Results are indicative of a decrease in surface area and pore volume due to inclusion of the POM species within the pores and channels of the parent silica supports. The reduction is much significant for the Preyssler POM as a result of its larger size compared to the Wells–Dawson complex.

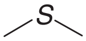
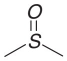
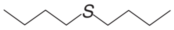
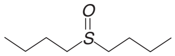
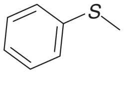
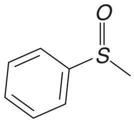
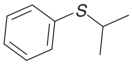
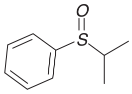
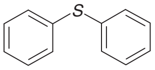
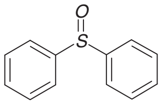
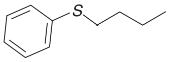
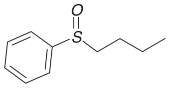
The amount of POM incorporated within the supports is estimated based on atomic adsorption data (Table 1). Loading differences are likely due to molecular sieve structure differences and results exhibit the effect imposed by texture and functional groups present at the surface and inside the pores of support. In case of $SBA\text{-}3/P_5$, small pores of SBA-3 hinder the diffusion of large P_5 species [17] and hence, guest POM molecules are expected to be mostly adsorbed on the external surface of the silica particles. Interestingly, higher loading is evidenced in MCM-48, compared to SBA-15, which may be explained based on its three-dimensional pore system compared to the one dimensional SBA-15 [36]. As anticipated, the amount of incorporated guest species is elevated after functionalization. Besides, presence of the positively charged NH_3^+ groups enhances the immobilization quality due to its strong ionic interactions with the negatively charged POM sphere. Hence, much stronger and stable interactions are expected in $[SBA/NH_3^+]/P_5$.

3.2. Catalytic performance of the designed systems

In order to clarify the catalytic active sites for oxidation of thioethers, blank reactions are carried out with bare silica supports under identical conditions. Pristine mesoporous materials are shown to be inert, with negligible yield and no conversion is achieved in the absence of catalysts. This implies that POM species serve as catalytic active positions.

All the newly designed hybrid catalysts are shown to be highly active and selective for oxidation of thioethers to sulfoxides with some of them being more efficient (Table 3). Results reveal that catalytic efficiency may be enhanced as the POM structure is enlarged and the number of tungsten atoms is increased. Actually, P_5 heterogeneous systems are found to be better catalysts for sulfoxide production, compared to their P_2 counterparts (Table 3 and Fig. 3). In fact,

Table 3
Catalytic performance of the designed mesoporous hybrid catalysts for oxidation of thioethers (* = TON (turnover number) is defined as mmol of sulfoxide/mmol POM).

Catalyst	Substrate	Product	Time (min)	Sulfoxide yield (%)	Selectivity (%)	TON*
SBA-15/P$_2$			30	96.6	97	621.1
SBA-15/P$_5$				96.3	96	1203.7
SBA-15/P$_2$			60	92.1	94	592.2
SBA-15/P$_5$				93.4	95	1167.4
SBA-15/P$_2$			60	96.9	98	623.03
SBA-15/P$_5$				97.5	98	1218.7
SBA-15/P$_2$			180	88.2	91	567.1
SBA-15/P$_5$				91.7	93	1146.2
SBA-15/P$_2$			180	92.4	95	594.1
SBA-15/P$_5$				94.1	97	1176.2
SBA-3/P$_5$			240	73.7	91	1355.3
MCM-48/P$_5$				80.5	90	888.2
SBA-15/P$_5$				90.3	96	1128.7
SBA-15/P$_2$				84.7	94	543.9
[SBA-15/NH_3^+]/P$_5$				95.9	98	700.6

the large oval-shaped P$_5$ complex, with higher number of tungsten atoms, allows effective and stable electron distribution and provides more available active sites that are likely to render the catalyst effectiveness [15].

Silica framework is also known to play an indispensable role in efficiency of mesostructured catalysts. To study the effect, butylsulfanylbenzene (BSB), a relatively large substrate, is oxidized in presence of the designed catalysts. The reaction procedure is closely monitored (Fig. 3). The order of sulfoxide yield is shown to follow the order: [SBA-15/NH_3^+]/P$_5$>SBA-15/P$_5$>MCM-48/P$_5$>SBA-3/P$_5$. The trend may be somewhat justified regarding the amount of P$_5$ immobilized within the support. However, closer monitoring of the oxidation procedure reveals that there may be some other effects taking part. As mentioned earlier, SBA-3 is known to have higher microporosity and smaller pore size and P$_5$ guest species are mostly adsorbed on the surface of the support. Hence, the thioether substrate is oxidized on the surface of SBA-3/P$_5$ catalyst and the reaction proceeds fast but less sulfoxide is produced. As for MCM-48/P$_5$, the reaction may be divided into two steps: oxidation on the catalyst surface where the adsorbed species are engaged and the reaction proceeds fast, and a slower step which occurs inside the pores. This behavior is attributed to the diffusional constrains usually present when a catalyst is supported inside the porous materials [20]. Regarding the diameter of MCM-48 pores, P$_5$ intercalation is somewhat expected to block the pores and produce hindrance for diffusion of BSB molecules. Hence, facile contact of reagents with the active catalytic sites is avoided and oxidation process is decelerated. As for the SBA-15 based catalysts, large pores and channels of the mesoporous support allows both incorporation of the relatively large P$_5$ species and fast diffusion of reagents. Hence, oxidation of BSB is selectively catalyzed inside copious pores and channels of the heterogeneous catalyst.

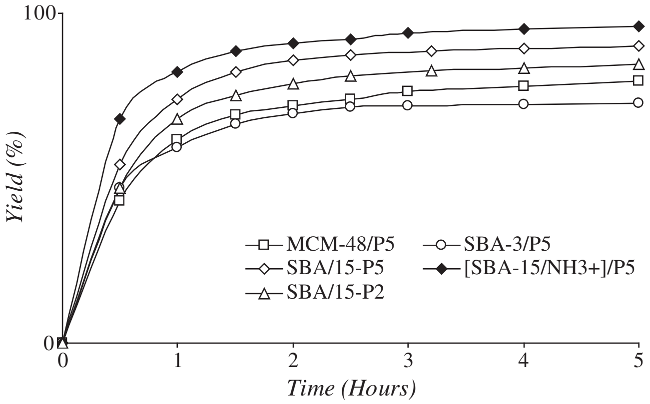


Fig. 3. Comparison of catalytic activity of heterogeneous mesostructured catalysts for oxidation of BSB.

As mentioned earlier, functionalization improves sorption properties and indeed, higher amount of active catalytic sites are more finely dispersed via chemical immobilization within NH_3^+ functionalized support. This elevates the catalyst's activity and gives rise to much efficient catalyst (Fig. 3).

To assess stability and reusability, catalysts are separated from the reaction mixture after each experiment, washed several times with dichloromethane and dried before being applied in the subsequent run. During the second cycle of reaction with SBA-3/P$_5$, MCM-48/P$_5$, and SBA-15/P$_5$ catalysts, 8.5%, 5.4%, and 4.3% reduction is evidenced (Fig. 4) in the sulfoxide yield. This may be attributed to leaching of unstable immobilized P$_5$ and the leaching is more pronounced when the guest is adsorbed on the surface. Nevertheless, the catalytic activity is nearly retained during the later runs. However, nearly no activity loss is evidenced with [SBA-15/NH_3^+]/P$_5$. Comparing the heterogeneous systems, it becomes evident that [SBA-15/NH_3^+]/P$_5$ is the most stable due to strong chemical interactions between the catalytic active sites and the supports and its catalytic property is nearly fully retained after at least 4 cycles (Fig. 4).

Although reusability is an important concept of heterogeneous catalysis, recycling tests are not sufficient proof of the heterogeneity of systems. To assess heterogeneity of systems, a procedure similar to Sheldon et al. [37] is performed and the catalysts are filtered after 30 min of reaction and the filtrate is allowed to react further. In case of [SBA-15/NH_3^+]/P$_5$, the liquor did not react further, and negligible change in the reaction coordinate is evidenced for SBA-15/P$_5$ and MCM-48/P$_5$ systems. However, in SBA-3/P$_5$ system, the reaction

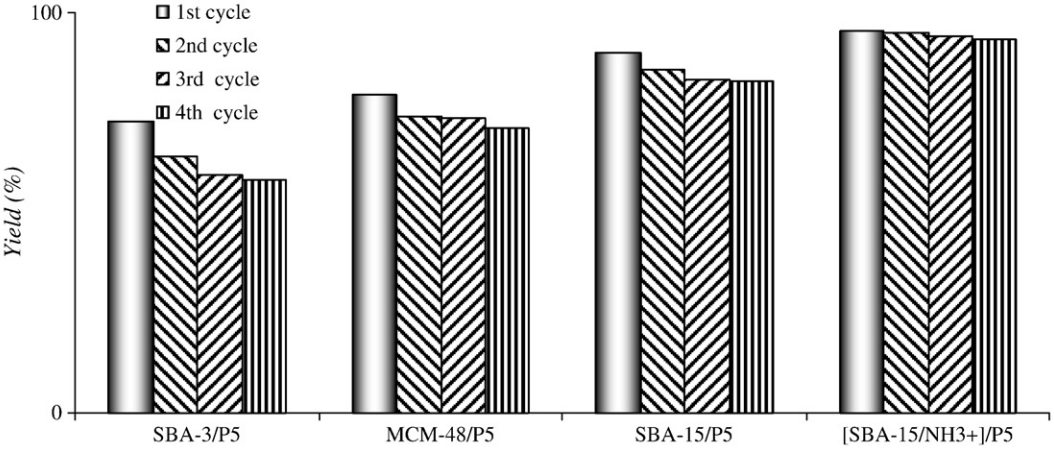


Fig. 4. Catalysts' reusability assessment for oxidation of BSB.

proceeds with a very slow pace after catalyst removal. This may be a sign for some unwanted release of POM. In order to shed light on the situation, the filtrate is analyzed for presence of tungsten species, using atomic absorption analysis. 0.31 mg tungsten is shown to be present in the filtrate which confirms the hypothesis of leaching in SBA-3/P_5 system. However, the leaching is not so significant and this explains the slow reaction in the absence of catalyst.

4. Conclusion

Inorganic–organic hybrids are designed by inclusion of $K_6P_2W_{18}O_{62}$ Dawson and $K_{14}[NaP_5W_{30}O_{110}]$ Preyssler salts within MCM-48, SBA-3, SBA-15 and NH_3^+ functionalized mesoporous silicas. The newly designed heterogeneous systems are shown to combine catalytic activity of POM with high surface area of mesoporous supports. Such kind of materials can be efficiently used as environmentally benign and selective heterogeneous catalysts for oxidation of thioethers to sulfoxides. The Preyssler complex is found to be a more active catalyst compared to its Dawson analog. The size of pores and functional groups present on the surface and within the pores and channels of the silica support is shown to be a determining factor for oxidation efficiency, stability, and reusability of the catalysts. Catalysts with larger pores are proven to be better catalysts for oxidation of relatively large thioethers. NH_3^+ functional group is shown to improve the sorption properties of the support and elevate the catalyst's activity and stability. Reusability investigations indicate that all the newly designed systems are heterogeneous and reusable. However, [SBA-15-NH_3^+]/P_5 is proved to be the superior heterogeneous catalyst for oxidation of thioethers, which may be recovered at least for 4 runs without any significant loss in activity. Heterogeneity of the newly designed catalysts is also studied. The systems are shown to be heterogeneous with some being more efficient.

Acknowledgment

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