Construction of Amphiphilic Polyoxometalate Supported on Amino-functional Ordered Meso/Macroporous SiO$_2$ and Its Catalytic Performance in Oxidative Desulfurization

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Abstract. Amphiphilic polyoxometalate was successfully immobilized on the surface of amino-functional ordered meso/macroporous silica materials by the precipitation method and used as a catalyst for oxidative desulfurization (ODS). The as-prepared catalyst exhibited highly ordered meso/macroporous structure with the amphiphilic polyoxometalate covered on the amino-functional SiO$_2$. The nanocomposite was used as catalyst in ODS process which can remove dibenzothiophene (DBT) in model fuel within 2 h. Moreover, the recyclability of catalysts was carried out and it was related to the increasing amino group on surface of catalyst.

1. Introduction

Deep desulfurization of fuel oils has been an essential process in petroleum refining process [1]. Conventional hydrodesulfurization was highly efficient in removing most of aliphatic and acyclic sulfur-containing compounds [2], however, it was less effective for DBT and its alkyl derivatives due to the high stereo hindrance [3]. In order to remove these refractory sulphur-containing compounds, alternative techniques, such as selective adsorption, ODS, biodesulfurization and extraction [4] have been explored. The ODS, due to the mild operation conditions, was considered to be one of the most promising method to achieve deep desulfurization. Keggin-type of polyoxometalate (POMs) showed superior catalytic activity for oxidation of sulfur-containing compounds in ODS system [56]. Porous carries such as MCM-41 [7], Ti molecular sieves [8], TiO$_2$ [9], have been developed to support POMs and used as catalyst for ODS. However, solvent which was used to extract the oxidation products of DBT and its alkyl derivatives was always needed in those heterogeneous systems and the regeneration of the solvent also will increase the cost [10]. Hence, amphiphilic polyoxometalate such as ionic liquid-modified HPW/SBA-15[11], supported SiW$_{12}$O$_{40}$-based ionic liquid [10], and MCM-41 supported (C$_{19}$H$_{42}$N)$_{2}$H$_{3}$(PW$_{11}$O$_{39}$) [12] were developed to achieve the solvent-free ODS system. Among these catalysts, amphiphilic POMs prepared by polyoxometalate anions and quaternary ammonium cations such as (C$_{19}$H$_{42}$N)$_{2}$H$_{3}$(PW$_{11}$O$_{39}$) supported on MCM-41 exhibited poor reusability in the ODS process. Luo GQ et al. successfully immobilized HPW on the surface of mesoporous MCM-41 modified by amino groups, the obtained catalyst showed excellent reusability in ODS system due to the strong interaction between the amino groups and the HPW molecules on the surface of MCM-41 [13].

In our previous study [141516], meso-macrostructured HPW/SiO$_2$ and HPW/TiO$_2$ material were prepared and used as ODS catalyst, which showed superior ODS activity than...
corresponding mesoporous catalysts. This should be attributed to the meso-macrostructure of catalyst which facilitated the mass transfer of reactants and products through the porous channels. In present work, amphiphilic POMs was successfully supported on the amino-functional SiO$_2$ in order to increase the solubility and cyclic capacity of active component loaded on catalyst. Its catalytic performance was investigated in ODS process.

2. Experimental

2.1. Preparation of amino-functional SiO$_2$

The ordered meso/macroporous SiO$_2$ support was synthesized through colloidal crystal template method [15]. Surface modification of ordered meso/macroporous SiO$_2$ was achieved via post-synthesis grafting method [17]. 1g as-synthesized SiO$_2$ was dispersed in 25 ml dry toluene with continuous stirring under N$_2$ atmosphere. Then, a known mount of APTES (0.5-5.0 mmol) was added into the solution and subjected to stirring at 110 °C for another 10h. The solid product was collected by filtration, then washed 3 times with 2-propanol and dried at 100°C overnight. The obtained material were designated as mSiO$_2$ (m stands for APTES usage).

2.2. Preparation of nCTA-POM /mSiO$_2$

x-SiO$_2$ supported CTA-POM was prepared by a co-precipitation method. 1 g mSiO$_2$ was dispersed into 50 mL deionized water. Then a certain amount of CATB (n$_{CTAB}$ : n$_{HPMo}$=3:1) dissolved in 10 ml deionized water was added to the suspension solution and stirred for 30 min, then 5 ml deionized containing desired amount of HPMo in water was added dropwise and subjected to stirring for another 2 h. Subsequently, the obtained green yellow precipitate was aged for another 5 h at 60°C. The suspension solution was separated by filtration, washed with deionized water, and then dried overnight. The obtained material was named as nCTA-POM/mSiO$_2$ (n stands for CTA-POM wt. %).

2.3. Oxidative desulfurization of model fuel

All model fuels (500 ppm S) were prepared by DBT, BT and 4,6-DMDBT dissolving in petroleum ether, respectively. In a typical run, 10 mL of model oil and a certain amount of catalyst were added into flask and heated to the desired temperature. Then, a certain amount of H$_2$O$_2$ was added to the flask to run the reaction. The dosage of oxidant was marked as O/S (the molar ratio of H$_2$O$_2$ to sulfur). After stirring for 2 h, the catalyst was centrifuged, washed with methanol for 3 times, dried overnight, and then subjected to the next run. The model fuel was withdrawn and analyzed by HPLC.

3. Results and discussion

The amount of aminopropyl functional group of modified support was indirectly measured by ICP analysis, Figure 1 showed the surface area and N content of amino-functional materials with respect to the APTES usage. The surface area of the silica decreased with the increasing APTES usage which attributed to blocking of micropores without changing the pore structure [18]. Meanwhile, the N content of modified silica was roughly increased, indicating that the aminopropyl group have successfully grafted on SiO$_2$. However, no obvious decease of surface area or additional increase of N content can be observed when APTES usage up to 2.0 mmol. The wild angle XRD patterns of catalysts indicated that the amphiphilic polynoxometalate has successfully dispersed in the silica framework. As shown in Figure 2, all samples exhibited a broad and wide diffraction peak at 24.3° and a weak one at 43.6°, assigned to amorphous silica [19]. There were no characteristic crystal diffraction peaks of HPMo were found in these samples, which demonstrated that the CTA-HPMo has dispersed homogeneously in SiO$_2$ framework and the increasing HPMo content does not affect the dispersion level [20]. Furthermore, the long-range ordering of mesopores was further examined by small-angle XRD patterns, there was a well-resolved diffraction peak on 2θ ~ 1.1° for sample 15CTA-POM/2.0SiO$_2$, characteristic of the periodic mesoporous structure.
Figure 1. Surface area and N content of SiO$_2$ as a function of the amount of APTES used

Figure 2. The wide-angle XRD patterns of (a) 10CTA-HPMo/2.0SiO$_2$, (b) 15CTA-HPMo/2.0SiO$_2$, (c) 25CTA-HPMo/2.0SiO$_2$ and the small-angle XRD patterns of 15CTA-HPMo/2.0SiO$_2$.

Subsequently, SEM analysis was used to investigate the surface morphologies of as-prepared samples. It can be seen from Figure 3 that all samples displayed a three-dimensionally ordered macroporous structure and the size of the macropore was about 270 nm, in accordance with the literature [15]. The mean pore size of macropores was 32% smaller than the diameter of the original PS (400 nm), suggesting significant shrinkage of the PS microspheres and condensation of silica framework during the calcination process [21]. With the increasing dosage of catalytically active components, it can be observed that the amphiphilic polyoxometalate was finely dispersed on the surface of the support and the macropores was blocked gradually (Figure 3 A-C). Furthermore, the mesopore character of catalysts was evaluated by TEM, as shown in Figure 2 two-dimensional (2D) hexagonal (p6mm) mesostructures permeating throughout the whole 15CTA-POM/2.0SiO$_2$ sample (Figure 4). As shown in Figure 4B, the macropore framework silica was composed of hexagonally-packed concentric mesophase channels, caused by the self-assembly of block copolymer solution around colloidal PS beads [22]. In addition, the measured mesopore size was roughly estimated to be 5 nm, which was in accordance with the XRD result.
Figure 3. SEM images of (a) 10CTA-HPMo/2.0SiO$_2$, (b, d) 15CTA-HPMo/2.0SiO$_2$ and (c) 25CTA-HPMo/2.0SiO$_2$.

Figure 4. TEM images of the 15CTA-HPMo/2.0SiO$_2$ sample.

Figure 5 showed the N$_2$ adsorption/desorption isotherms and pore size distributions of nCTA-POM/2.0SiO$_2$ samples. All materials exhibited type IV adsorption isotherms with type-H2 hysteresis loops, indicating the existence of mesopores [23]. The height of the capillary condensation decreased with increasing CTA-POM, demonstrated that the amphiphilic polyoxometalate was supported on the surface of the silica matrix. Additional prominent hysteresis occurred at relative pressure $p/p_0 > 0.9$ can be attributed to the high concentration of macropores interconnected via mesopores [22]. The pore size displayed narrow distributions with mean pore size around 4.5 nm (Figure 4B), Table 1 showed the textural parameters of catalysts, surface area and pore volume of samples decreased with the increase of CTA-POM contents, related to a blockage of the pores of the support by excessed CTA-POM [19].
Figure 5. Nitrogen adsorption/desorption isotherms (A) and corresponding BJH pore size distribution curves (B) of amino-functional ordered meso/macroporous SiO$_2$ with different HPMo contents.

Table 1. The structure parameters and sulfur removal activities of catalysts.

| Catalysts                  | HPW dosage (%) | S$_{BET}$ (m$^2$/g) | D $^b$ (nm) | V$_t$ $^c$ (cm$^3$/g) | Sulfur removal $^f$ |
|---------------------------|----------------|----------------------|-------------|-----------------------|---------------------|
| 10CTA-HPMo/2.0SiO$_2$     | 8.9            | 145.6                | 4.52        | 0.36                  | 95.2%               |
| 15CTA-HPMo/2.0SiO$_2$     | 14.7           | 89.4                 | 4.50        | 0.31                  | 99.1%               |
| 25CTA-HPMo/2.0SiO$_2$     | 23.6           | 30.1                 | 4.49        | 0.11                  | 86.9%               |

$^a$ S$_{BET}$ BET specific surface area.

$^b$ D mesopore diameter at the maxima of BJH pore size distribution curve.

$^c$ V$_t$, total pore volume.

$^f$ Reaction conditions: catalyst dosage = 0.05 g, T = 60 °C, O/S = 4 and t = 80 min.

Figure 6 displayed the FT-IR spectra of amino-functional SiO$_2$, CTA-HPMo, and 15CTA-HPMo/2.0SiO$_2$ samples. A band appeared at 1630 cm$^{-1}$ was related to the -OH vibration of physisorbed H$_2$O in catalyst. The broad band observed between 2700 to 3400 cm$^{-1}$ and week peak in 1510 cm$^{-1}$ were assigned to the -NH$_3^+$ stretching vibration, which suggested the successful introduction of APTES on catalyst surface [18,24]. The Kegging structure of CTA-HPMo was confirmed by FT-IR spectres in 1064 cm$^{-1}$ (P-O band), 964 cm$^{-1}$ (Mo=O band), 868 cm$^{-1}$ (Mo-O-Mo bands) [2526]. However, pure SiO$_2$ displayed several typical bands at 805 cm$^{-1}$, 960 cm$^{-1}$ and 1060-1250 cm$^{-1}$ [14], which might overlapped with the bands of CTA-HPMo. There were still weak characteristic at 965 and 872 cm$^{-1}$ can be observed. Furthermore, CTA-HPMo content on the catalyst was investigated by ICP elemental analysis (Table 1). The contact angle of 15CTA-POM/2.0SiO$_2$ was calculated when a drop of water was contacted with the surface of 15CTA-HPMo/2.0SiO$_2$ sample. The contact angle showed in Figure 7 indicated that its amphiphilic. The amphiphilic of catalyst will facilitate the absorption process of both aqueous H$_2$O$_2$ and model oil, thus, enhanced the sulfur removal rate of catalyst [10].

Figure 6. FT-IR spectra of amino-functional SiO$_2$, CTA-HPMo, and 15CTA-HPMo/2.0SiO$_2$ samples.
The effect of loading amount of CTA-POM on the desulfurization rate was presented in Figure 8. The removal rate of DBT was enhanced dramatically when the catalyst dosage increased from 0-15 wt.%, this was because of the increasing total amount of catalytic active sites. However, the desulfurization rate declined dramatically when loading amount up to 25 wt.%, which can be attributed to the over much loading CTA-POM blocking the pore channel of the support [11]. Therefore, the future experiments will proceed with 15CTA-POM/2.0SiO$_2$ sample. The reusability of 15CTA-HPMo/mSiO$_2$ with different amount of APTES used was exhibited in Figure 9. Under same reaction condition, 15CTA-HPMo/2.0SiO$_2$ catalyst showed higher recycle ability than other catalysts, there was still 13.6 wt% PMo content on the catalyst surface. While, few PMo content of 15CTA-HPMo/0SiO$_2$ can be detected on the catalyst after 4 runs. These results indicated that the amino-function on SiO$_2$ may act as an important factor influencing the reusability of 15CTA-HPMo/mSiO$_2$ catalyst.

Figure 7. Contact angle for a water droplet a on the surface of 15CTA-HPMo/2.0SiO$_2$.

Figure 8. The effect of HPMo contents on the desulfurization rates, catalyst dosage = 0.05 g, T = 60 °C and O/S = 4.

Figure 9. The reusability of 15CTA-HPMo/mSiO$_2$ with different amount of APTES used. (a) 15CTA-HPMo/0SiO$_2$, (b) 15CTA-HPMo/0.5SiO$_2$, (c) 15CTA-HPMo/1.0SiO$_2$ (d) 15CTA-HPMo/1.5SiO$_2$ and (e) 15CTA-HPMo/2.0SiO$_2$. 
4. Conclusions
In summary, a series of amphiphilic polyoxometalate supported on amino-functional ordered meso/macroporous SiO$_2$ materials were synthesized by the precipitation method. The obtained material possessed highly ordered macroporous and ordered mesoporous structure with catalytically active components of amphiphilic polyoxometalate covered on the amino-functional SiO$_2$ catalyst surface. The amphiphilic polyoxometalate supported material behaved as homogeneous catalysts in ODS process and it displayed excellent ODS performance and recyclability. 500ppm DBT in model fuel was removed within 2 h under optimal condition. Moreover, the catalyst can be easily separated from ODS system and it showed excellent catalytic activity even after four cycles.

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6. References
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