Efficient and reusable ordered mesoporous WO<sub>x</sub>/SnO<sub>2</sub> catalyst for oxidative desulfurization of dibenzothiophene†

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The oxidative desulfurization (ODS) of organic sulfur compounds over tungsten oxide supported on highly ordered mesoporous SnO<sub>2</sub> (WO<sub>x</sub>/meso-SnO<sub>2</sub>) was investigated. A series of WO<sub>x</sub>/meso-SnO<sub>2</sub> with WO<sub>x</sub> contents from 10 wt% to 30 wt%, were prepared by conventional wet impregnation. The physico-chemical properties of the WO<sub>x</sub>/meso-SnO<sub>2</sub> catalysts were characterized by X-ray diffraction (XRD), N<sub>2</sub> adsorption–desorption isotherms, electron microscopy, Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and the temperature-programmed reduction of hydrogen (H<sub>2</sub>-TPR). The characterization results indicated that these catalysts possessed mesoporous structures with uniform pores, high specific surface areas, and well-dispersed polyoxotungstate species on the surface of meso-SnO<sub>2</sub> support. The ODS performances were evaluated in a biphasic system (model oil/acetonitrile, S<sub>total</sub> = 2000 ppm), using H<sub>2</sub>O<sub>2</sub> as an oxidant, and acetonitrile as an extractant. Dibenzothiophene (DBT) in the model oil was removed completely within 60 min at 50 °C using 20 wt% WO<sub>x</sub>/meso-SnO<sub>2</sub> catalyst. Additionally, the effect of reaction temperature, H<sub>2</sub>O<sub>2</sub>/DBT molar ratio, amount of catalyst and different sulfur-containing substrates on the catalytic performances were also investigated in detail. More importantly, the 20 wt% WO<sub>x</sub>/meso-SnO<sub>2</sub> catalyst exhibited 100% sulfur-removal efficiency without any regeneration process, even after six times recycling.

1. Introduction

Sulfur-containing compounds in transportation fuels are converted to SO<sub>x</sub>, which is a major source of air pollution and energy corrosion.† Thus, removal of sulfur has become an important research subject worldwide, and many countries have legislated environmental regulations that limit sulfur content in fuels to be below 10 ppm.‡ To date, hydro-desulfurization (HDS) is a conventional desulfurization method in the petroleum refining industry for the removal of sulfur in fuels, including thiols, thioethers, and disulfides. However, the HDS process has some respective disadvantages. For example, HDS requires severe operation conditions at high pressure of (20–100) atm of H<sub>2</sub> and temperatures (300–400 °C).‡ Additionally, it is difficult to remove refractory sulfides, such as benzo-thiophene (BT), dibenzothiophene (DBT), and their derivatives, owing to their steric hindrance, and low electron density around sulfur atom.‡ Therefore, alternative processes have been suggested to overcome these drawbacks. So far, several alternative deep desulfurization technologies, such as adsorption, extraction, bioprocess, oxidation and photocatalytic oxidation desulfurization have been extensively investigated.

Among these processes, oxidative desulfurization (ODS) combined with extraction process is considered to be one of the most promising processes. It can be operated at atmospheric pressure and low temperature without consuming hydrogen. During this process, organic sulfides can be oxidized into highly polar sulfones and sulfoxides by catalysts with suitable oxidants, and removed by the subsequent extraction process using polar organic solvents. Various oxidants have been used for the oxidation of sulfur compounds, including molecular oxygen, ozone, organic peroxide, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Among them, H<sub>2</sub>O<sub>2</sub> has been extensively used, due to its high activity, high oxidative capacity, and production of only water after the reaction.

In the field of heterogeneous catalysis, it is well-known that group 5 and 6 metals (e.g., Mo, W, V) in high oxidation states can react with hydrogen oxide to produce peroxometallate complexes, which are efficient catalysts for oxidative desulfurization reaction. Caero et al. examined the ODS of a real diesel fuel on V<sub>2</sub>O<sub>5</sub> supported on alumina, silica, niobia, ceria, and titania, and reported that an approximately 99% decrease...
in the initial amount of sulfur.25 Prasad et al. reported that MoO3/Al2O3-SiO2 catalyst had the best catalytic performance for ODS of 4,6-dimethylbenzothiphene (4,6-DMDBT) with tert-butyl hydroperoxide.26 A novel composite catalyst VₓMoO3/NC exhibited excellent ODS activity and reusability, which was ascribed essentially to the strong electron-donating effect of NC on VₓMoO3.27 Additionally, tungsten-based catalysts have also been extensively studied for ODS reaction in both single and biphasic liquid phase operating systems, due to the tungsten-oxide species on the surface of catalysts as active sites being combined with H2O2 to form peroxy-tungsten intermediates (W–O–O–H), contributing to the conversion of DBT to DBTO2 in the oxidation process.28 In order to improve the activity and stability of catalysts, tungsten species are dispersed on various supports such as W–MCM–41,27–29 WO3–SBA–15,30 WO3/TiO2,31 WO3–ZrO2,32 WO3/MoS2,33 and Mo/KIT-6-Ti.34

Recently, SnO2-based heterogeneous catalyst containing tungsten oxide has been reported, exhibiting efficient oxidation of amines and sulfides with green oxidant H2O2, has been reported.35 Zhang et al. have prepared WO3/SnO2 composite catalysts by the co-precipitation impregnation method for selective the oxidation of 1,2-benzenedimethanol to phthalide using H2O2 as oxidant, suggesting that high dispersion of tungsten species on SnO2 can improve catalytic activity in reaction.36 Ma et al. have found that the SnO2–WO3 composite as solid acid catalyst is more effective than pure WO3 and SnO2 catalysts in the hydrolysis of dichlorodifluoro-methane, due to the strong interaction between WO3 and SnO2. According to the above reports, SnO2 will be a good choice as support to disperse WO3 for ODS reaction. In the present work, highly ordered mesoporous SnO2 (meso-SnO2) was successfully prepared from KIT-6 silica template using a nano-replication method. WO3, SnO2, and WO3/SnO2 composite were dispersed on the meso-SnO2 support by an incipient wet-impregnation method. The Deep desulfurization performance of WO3/meso-SnO2 catalysts for fuel oil in a biphasic (model oil/acetonitrile) system under different reaction conditions was investigated in detail. The WO3/meso-SnO2 catalysts with 20 wt% WO3 loading showed excellent catalytic performance in removing DBT, BT, and 4,6-DMDBT, because when WO3 species interacted with SnO2, a lot of active species (tungsten oxo-species, W=O) were generated. Furthermore, the catalysts with high surface area, large pore size, and 3D pore network are beneficial for the diffusion and transport of reactants and products during ODS reaction. In addition, the reusability and stability of the catalyst was investigated.

2. Experimental

2.1 Synthesis of KIT-6 silica template

The typical synthesis of the mesoporous KIT-6 silica template was similar to the process described in the literature.35–37 A triblock copolymer (pluronic P123, EO20PO70EO20, Aldrich) was dissolved in distilled water and n-butanol solvent was added to the mixture at room temperature. The solution was vigorously stirred for 6 h to obtain a clear polymer solution. The clear solution was then kept in a water bath at 35 °C for 24 h followed by the addition of hydrochloric acid (HCl, Samchun) and tetraethylorthosilicate (TEOS, Samchun) with magnetic stirring. The molar composition of the mixture was P123 : BuOH : TEOS : HCl : H2O = (0.017 : 1.01 : 1.33 : 0.45 : 198). After that, the mixture was kept in an oven at 100 °C for another 24 h. The white precipitates were filtered and washed with distilled water and ethanol to completely remove the block copolymer. Finally, the product was calcinated at 550 °C for 3 h in air.

2.2 Synthesis of ordered mesoporous SnO2

Ordered mesoporous SnO2 (meso-SnO2) material was prepared by a nano-replication method using mesoporous KIT-6 as silica template. The meso-SnO2 material was synthesized by a solvent-free infiltration method.6 Typically, 5.09 g SnCl2·2H2O (Aldrich) was melted at 100 °C to liquid states. It was then impregnated into 5.0 g of preheated silica template. The composite materials were shaken for 1 h, and put in an oven at 80 °C overnight, in order to let the precursor spontaneously infiltrate into mesopores of the silica template. The composite material was then calcined at 700 °C for 3 h under static air condition. After that, the silica template was removed from the composite by a wet-etching process using a 20 wt% hydrofluoric acid (HF) solution. The resulting solid product was washed with distilled water and acetone several times, and then dried at 80 °C overnight in an oven.

2.3 Synthesis of WO3/meso-SnO2 catalysts

WO3-supported catalysts were prepared by an incipient wetness impregnation method. To obtain 20 wt% WO3/meso-SnO2, an aqueous solution of (NH4)6H2W12O40·xH2O (0.266 g, Aldrich) was impregnated into 1.0 g of meso-SnO2. After drying at 80 °C overnight, the obtained product was heated at 400 °C for 3 h under static air condition. WO3/meso-SnO2 with (10 and 30) wt% loadings were also prepared through the same method.

2.4 Characterization

The X-ray diffraction (XRD) patterns of these prepared catalysts were obtained from a Rigaku D/MAX-2200 ultima equipped with Cu Kz radiation (λ = 1.54 Å) at 30 kV and 40 mA. N2 adsorption–desorption isotherms were obtained using a Micromeritics Tristar system at liquid N2 temperature. Before measurements, samples were degassed at 323 K for 12 h. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were utilized to calculate the BET surface area and pore size distribution, respectively. Scanning electron microscopy (SEM) image was obtained using a Hitachi UHR S 5500 FE-SEM operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were collected using JEOL JEM 3010 at an accelerating voltage of 200 kV. Raman spectra were recorded under ambient conditions at room temperature (RT) using WITEC Alpha300. The excitation line of the laser was at 532 nm. Fourier transform infrared spectroscopy (FT-IR) spectra were measured using KBr wafer technique with Bruker IFS-66 spectrometer. H2-Temperature programmed reduction (H2-TPR) was performed in a fixed-bed reactor. Sample (20 mg) was put in a quartz microreactor, and pretreated with He up to
100 °C at a rate of 10 °C min⁻¹ for 1 h for pretreatment. Then 10 vol% H₂ in a He flow of 40 mL min⁻¹ was maintained at RT for 30 min. Finally, the sample was ramped to 900 °C at 10 °C min⁻¹.

2.5 Catalytic performance

Sulfur-containing compound (DBT, BT, or 4,6-DMDDBT) was dissolved in n-heptane using a corresponding S-content of 2000 ppm as model oil. A typical ODS reaction of model oil was carried out in a 100 mL two-necked flask by adding 0.1 g catalyst, 0.27 mL of 34.5% H₂O₂ aqueous solution, 14 mL of acetonitrile, and 14 mL of the model oil successively into the flask, followed by vigorously mixing with a magnetic stirrer at 50 °C for 2 h under atmospheric pressure. Reaction products (upper oil layer) were analyzed by gas chromatography–flame ionization detector (GC–FID) equipped with a HP-5 capillary column (30 m × 0.32 mm inner diameter × 1.0 μm film thickness).

3. Results and discussion

3.1 Catalyst characterization

Fig. 1 shows the low- and high angle XRD patterns for the KIT-6 template (inset), meso-SnO₂, and WO₃/meso-SnO₂ materials. In the low-angle XRD patterns (Fig. 1A), KIT-6 exhibited typical diffraction peaks (211), (220), and (332), which are characteristic of the cubic Ia₃d mesostructure. The meso-SnO₂ and WO₃/meso-SnO₂ materials exhibited two narrow and well-defined peaks (110) and (211), indicating the highly ordered mesostructure of all materials. The presence of new diffraction peak (110) around 0.60° indicated that after the silica template etching process the cubic Ia₃d mesostructure of KIT-6 silica template transformed into tetragonal I₄₁/a (or lower symmetry). In the wide-angle XRD patterns (Fig. 1B), diffraction peaks of meso-SnO₂ with 2θ/degree values corresponding to (110), (101), (200), (211), (220), (002), (310), (301), (202), and (321) planes exhibited a typical tetragonal phase of SnO₂ (ICPDS 21-1250, P4₁/mmm). After loading (10 and 20) wt% WO₃ on meso-SnO₂, there was no diffraction line of the tungsten oxide species in wide angle patterns, revealing that the WO₃ existed mainly in amorphous phases or particles size was very small, and they were finely dispersed on the meso-SnO₂ support. The Diffraction peaks of crystalline WO₃ appeared when 30 wt% WO₃ was loaded on meso-SnO₂, as shown in Fig. 1B. Table 1 summarizes the crystallographic properties of meso-SnO₂ and WO₃/meso-SnO₂ materials and shows that after loading different amounts of WO₃ on meso-SnO₂ support, the surface areas, pore volumes, and pore sizes of samples were decreased, probably due to the partial pore blockage by the impregnated WO₃. Compared to the calcined meso-SnO₂, pure meso-SnO₂ combined with WO₃ could suppress the particle agglomeration during the sintering process, due to the cooperative nature of the cations of the mixed oxides.²

The SEM (Fig. 2a–d) and TEM images (Fig. 2e–h) also confirm the meso-SnO₂ and WO₃/meso-SnO₂ materials with regular porosity and well-defined crystalline frameworks. All the materials consisted of well-defined nanopores and frameworks with uniformly repeating units over the whole particle, indicating that the highly ordered mesostructure remained before and after loading works. The W/Sn ratios of the WO₃/meso-SnO₂ materials with different amounts of WO₃ loading were obtained by Energy dispersive X-ray spectroscopy (EDX) from SEM analysis (Table 1), indicating that the tungsten content increased with increasing the amount of WO₃ loading. High-resolution TEM images (inset of TEM images) indicated that the meso-SnO₂ and (10 and 20) wt% WO₃/meso-SnO₂ materials exhibited well-formed crystalline framework structures. The d-spacings of 3.41, 2.68 and 2.35 Å correspond to the (110), (101) and (200) planes of the tetragonal phase of SnO₂, indicating that the WO₃ was finely dispersed on the surface of meso-SnO₂, without aggregation. Fig. 2h shows that the catalyst with 30 wt% WO₃ loading mainly displayed the crystal SnO₂ structure with tiny WO₃ structure with d-spacing of 3.85 Å, which was indexed to the (001) plane of the orthorhombic WO₃ phase. EDX mapping images obtained from TEM analysis revealed that the tungsten atoms in WO₃/meso-SnO₂ materials were homogeneously dispersed over the whole particles as shown in Fig. 2j–l.

Fig. 3 shows the Raman spectra of meso-SnO₂ and WO₃/meso-SnO₂ materials in the spectral range of 200 to 1200 cm⁻¹.
The spectrum of meso-SnO₂ showed the bands at around 476 cm⁻¹ (Eg), 633 cm⁻¹ (A₁g), and 774 cm⁻¹ (B₂g) that could be assigned to the tetragonal structure of SnO₂.44 After loading tungsten species, the prominent A₁g band was shifted to higher wave numbers than that of pure meso-SnO₂, indicating the presence of interaction between WOₓ species and SnO₂.45 Simultaneously, the broad band appeared in the 200–400 cm⁻¹ region was attributed to the W–O–W bending modes.46 The new band at around 960–980 cm⁻¹ appeared in all the WOₓ/meso-SnO₂ materials was attributed to the terminal W=O bonds of surface WOₓ species. The shift of surface W=O band from 960 cm⁻¹ to 980 cm⁻¹ with increasing the WOₓ loading might be related to the polymerization of surface monooxo tungsten species.47 With further increase in WOₓ loading (30 wt%), three new bands at about 272 cm⁻¹, 715 cm⁻¹ and 807 cm⁻¹ were observed. This can be assigned to asymmetric and symmetric stretching vibration of W–O–W modes and W=O streatching modes. It is noteworthy that the formation of crystalline WO₃ phase as observed in XRD and TEM measurements.48

The FT-IR spectra of meso-SnO₂ and the WOₓ/meso-SnO₂ materials with different WOₓ contents are presented in Fig. S2.49 As reported in the literature,49 the peaks at 651 cm⁻¹ and 553 cm⁻¹ could be assigned to different vibration modes of O–Sn–O and Sn–O–Sn groups. For WOₓ/meso-SnO₂ materials,
a peak appeared at 970 cm$^{-1}$ was assigned to the stretching modes of W–O bond or W=O bond. Another new peak at 868 cm$^{-1}$ demonstrated the typical Sn–O–W modes, indicating the presence of strong interactions between highly dispersed WO$_x$ and meso-SnO$_2$. Additionally, the peak at 1621 cm$^{-1}$ was attributed to the bending vibrations of hydrogen-bonded surface OH groups of physically adsorbed water molecules.$^{31}$

H$_2$-TPR was examined to investigate the reducibility of meso-SnO$_2$ and WO$_x$/meso-SnO$_2$ catalysts. As shown in Fig. 4, the TPR profile of bulk WO$_3$ exhibited two high intensity peaks of hydrogen consumed beginning at 600 °C, centered at 770 and 870 °C. It is important to note that these peaks might be assigned to the stepwise reduction of WO$_3$ to W [WO$_3$ → W$_{20}$O$_{58}$ → WO$_2$ → W].$^{32}$ The TPR profile of pure meso-SnO$_2$ exhibited a mainly reduction peak at about 652 °C, which could be assigned to the reduction of Sn(4+) → Sn(2+) → Sn(0). After impregnated WO$_x$, the first reduction peaks of all the WO$_x$/meso-SnO$_2$ catalysts shifted to lower temperature, indicating the presence of interaction between WO$_x$ species and meso-SnO$_2$ support. Simultaneously, the relative area of this reduction peak increased with increasing WO$_x$ concentration due to the increasing fraction of WO$_x$ species in domains. The reduction temperature of the first peak at 450–550 °C was probably attributed to the reduction of octahedrally coordinated WO$_x$ species as reported by Wachs et al.$^{33}$ Octahedrally coordinated WO$_x$ species were found to be reduced at temperatures varying from 300 to 600 °C through intermediate oxidation states. Accordingly, the reduction peaks at 450–700 °C were assigned to the WO$_3$ to WO$_{2.9}$ (or WO$_2$) reduction process and the reduction of SnO$_2$. The other two peaks located at higher temperature between 740 °C and 900 °C were probably attributed to a further reduction process of partially reduced WO$_x$ species (WO$_{2.9}$ → WO$_2$ → W) formed in the first reduction peak, together with the reduction of tetrahedrally coordinated WO$_x$ species that interacted with SnO$_2$ support.$^{34,55}$ In the case of 30 wt% WO$_x$/meso-SnO$_2$ catalyst, there were three reduction peaks centered at 743, 770, 867 °C, similar to those of bulk WO$_3$, indicating the formation of crystalline WO$_3$ on the surface of meso-SnO$_2$ support. In the case of 30 wt% WO$_x$/meso-SnO$_2$ catalyst, there were three reduction peaks centered at 743, 770 and 867 °C, similar to those of bulk WO$_3$, indicating the formation of crystalline WO$_3$ on the surface of meso-SnO$_2$ support.

### 3.2 Catalytic study

Fig. 5 shows the catalytic performance of pure meso-SnO$_2$ and WO$_x$/meso-SnO$_2$ catalysts for the removal of DBT from model oil, which were carried out at 50 °C with H$_2$O$_2$ as oxidant for 2 h.

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**Fig. 4** H$_2$-TPR Profiles of (a) meso-SnO$_2$, (b) 10 wt% WO$_x$/meso-SnO$_2$, (c) 20 wt% WO$_x$/meso-SnO$_2$, and (d) 30 wt% WO$_x$/meso-SnO$_2$.

**Fig. 5** Effect of different catalyst on removal of DBT from model oil. Reaction conditions: mode oil = 14 mL, acetonitrile = 14 mL, sulfur concentration = 2000 ppm, catalyst = 0.1 g, n[H$_2$O$_2$] : n[S] = 5 : 1, reaction temperature = 50 °C, time = 60 min.

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**Fig. 6** Effect of (a) reaction temperatures, (b) molar ratio of H$_2$O$_2$/S, and (c) amount of catalyst on removal of DBT from model oil over 20 wt% WO$_x$/meso-SnO$_2$ catalyst reaction conditions: model oil = 14 mL, sulphur concentration = 2000 ppm, catalyst = 0.1 g, n[H$_2$O$_2$] : n[S] = 5 : 1, time = 60 min.
WOx supported catalysts (WOx/meso-SnO2) exhibited better catalytic performance than pure SnO2 support because the surface tungsten–oxygen species (W=O) as the active sites could interact with H2O2 to form surface peroxy-tungsten (W=O–O–H) species, and then DBT was oxidized to DBTO2 via oxidation process. Therefore, the amount of WOx loaded on meso-SnO2 immensely influenced the desulfurization efficiency. As shown in Fig. 5, the desulfurization efficiency of WOx-supported catalysts was remarkably increased with increasing WOx concentration and reached the 100% removal with 20 wt% WOx loading. The reason is because the active sites of tungsten–oxygen species of 20 wt% WOx/meso-SnO2 catalyst are more than those of other catalysts. Further increase the WOx loading up to 30 wt% resulted in the decrease catalytic removal of DBT (94.5%). This phenomenon may be ascribed to the excess of 20 wt% WOx caused agglomeration of tungsten oxide on the surface of meso-SnO2 and the formation of crystalline WO3 lead to a smaller surface area as shown in BET results (Table 1).

In order to examine the influence of reaction temperatures on the removal of DBT, a series of experiments were performed at different temperatures using 20 wt% WOx/meso-SnO2 catalyst. As shown in Fig. 6(a), raising the reaction temperature from 20 °C to 50 °C resulted in a remarkable increase in DBT removal efficiency and complete removal at 50 °C after 60 min. This indicates that the higher temperature is beneficial for H2O2 oxidation because the higher oxidation reaction rate at low temperatures might be limited by kinetics. According to the above analysis, 50 °C was chosen as the optimal reaction temperature in this work.

H2O2 is one of the main factors in oxidative system. Hence, oxidative desulfurization of DBT was carried out under different molar ratios (from 2 to 10) of H2O2/S at 50 °C with 20 wt% WOx/meso-SnO2 as catalyst. As shown in Fig. 6(b), the DBT removal efficiency was increased with increasing the molar ratio of H2O2/S from 2 to 5 followed by a slight decreased at molar ratio of 10. This indicates that the excess oxidant is beneficial for increasing the reaction efficiency in heterogeneous catalysis. According to the stoichiometry of the ODS reaction, 2 mole of H2O2 are consumed for the conversion of 1 mole of sulfur-containing compounds to their corresponding sulfones (DBTO2). However, the molar ratio of 2 gives only 90.3% of the sulfur removal, whereas the DBT can be removed completely from the model oil at the H2O2/S molar ratio of 5. The optimum ratio of H2O2/S was found to be 5, indicating that the H2O2 not only reacting with DBT, but also taken its self-decomposition. Therefore, stoichiometric amount of H2O2 can not result in complete oxidation of DBT under the present reaction conditions.

The amount of catalyst also affects desulfurization efficiency on the removal of DBT. As shown in Fig. 6(c), the sulfur removal increased from 74.7% to 100% in 60 min, when the amount of catalyst increased from 0.02 to 0.1 g. Below 0.1 g catalyst amount, the active sites of the catalyst were not enough to catalysis oxidative oxidize DBT completely. Nevertheless, when the catalyst amount increased to 0.15 g, the removal efficiency for DBT decreased to 97.2%. Therefore, the excessive catalyst was unnecessary in the desulfurization reaction because the excess active sites of catalyst might be covered by the absorption and aggregation among the catalyst in a certain reaction volume, resulting the limitation of active sites actually contacted with sulfur-containing compound. Thus, 0.1 g catalyst was chosen as the optimal amount for ODS reaction.

To study the effect of different sulfur-containing compounds in ODS reaction over 20 wt% WOx/meso-SnO2 catalyst. Beside DBT, benzothiophene (BT), and 4,6-dimethyl-dibenzothiophene (4,6-DMDDBT), are also inflexible to be removed from fuels. The results in Fig. 7(a) indicated that the catalytic activity of these sulfur-containing compounds decreased in the order of DBT (100%) > 4,6-DMDDBT (99.2%) > BT (94.4%) under the same experimental conditions. It may be ascribed to the different electron density of sulfur atoms on BT (5.739), DBT (5.758), and 4,6-DMDDBT (5.760). In general, lower electron density on sulfur atom resulted in lower activity of the sulfur removal rate. Therefore, the lower electron density of sulfur atom on BT directly resulted in lowest surff removal efficiency. Moreover, compared to DBT, 4,6-DMDDBT with two methyl groups on the benzene caused steric hindrance effect, leading to the active species hard to approach the sulfur atom. Therefore, the desulfurization efficiency of 4,6-DMDDBT was lower than that of DBT.

To understand ODS kinetics, the kinetics parameters of DBT oxidation at different temperatures (20 °C, 30 °C, 40 °C, and 50 °C) were studied. The rate constants for the apparent consumption of DBT were obtained from the pseudo-first-order equation:

$$\ln(C_0/C_t) = kt$$  (1)

wherein, $C_0$ and $C_t$ were the sulfur concentrations at time zero and time $t$ (min), respectively, $k$ was the rate constant (min$^{-1}$). As shown in Fig. S3(A†), a plot of $\ln(C_0/C_t)$ versus reaction time ($t$) displayed a linear relationship that confirmed the pseudo-first order reaction kinetics. The apparent rate constants of DBT were 0.0008, 0.016, 0.036 and 0.063 min$^{-1}$ at 20 °C, 30 °C, 40 °C, and 50 °C, respectively. Based on the reaction rates at different temperatures, the apparent activation energy of DBT oxidation was derived from the Arrhenius equation:

$$E_a = RT^2(\frac{d\ln k}{dT})$$  (2)

$$t_{1/2} = 0.693/k$$  (3)
where, $E_a$ is the apparent activation energy, $R$ and $T$ are the gas constant and reaction temperature, respectively. Through the Arrhenius plot as shown in Fig. S3(B),† the activation energy of DBT is 54.8 kJ mol$^{-1}$. Zhu et al.$^{18}$ have reported that the activation energy of DBT is 76.2 kJ mol$^{-1}$ in the polyoxometalates/H$_2$O$_2$ catalytic system. In AcOH/H$_2$SO$_4$/H$_2$O$_2$ system the activation energy of DBT oxidation is 57 kJ mol$^{-1}$, reported by Ukkirapandian et al.$^{14}$ The oxidation kinetics of BT and 4,6-DMDBT were also investigated under the optimal conditions. The plot of ln($C_0/C$) versus time is shown in Fig. 7(b). Half-life was calculated by eqn (3). The rate constants $k$ of DBT, BT, and 4,6-DMDBT were 0.0631 min$^{-1}$, 0.0260 min$^{-1}$, and 0.0458 min$^{-1}$, respectively. The half-life $t_{1/2}$ and correlation coefficients $R$ are summarized in Table 2.

Reusability and stability of the catalyst are very important factors in industrial applications. Therefore, the reusability of the catalyst for DBT removal was investigated over 20 wt% WO$_x$/meso-SnO$_2$ catalyst. Each run, the used catalyst without any treatment (i.e., solvent washing, recalcination) was separated from the reaction mixture by centrifugation. Then, fresh H$_2$O$_2$ and model oil were directly added into the original reaction round-bottom flask for the next run. Fig. 8(a) showed that the sulfur removal efficiency remained at 100% after recycling for 6 times. This is because the active tungsten species are present on the surface of meso-SnO$_2$ after recycling ODS reactions, as shown in the Fig. 8(b) Raman spectra. The results indicated that the 20 wt% WO$_x$/meso-SnO$_2$ has an excellent recycling performance in the deep oxidation desulfurization.

4. Conclusions

Highly ordered mesoporous WO$_x$/meso-SnO$_2$ catalysts with high surface area and well-defined mesoporosity were successfully prepared by the nano-replication method and applied to oxidative desulfurization reaction for the first time. In this ODS system, through the optimization of reaction conditions, sulfur removal of DBT could reach 100% under 50 °C with 20 wt% WO$_x$/meso-SnO$_2$ as catalyst. Furthermore, 20 wt% WO$_x$/meso-SnO$_2$ catalysts also exhibited excellent recycling performance after recycling six times without losing catalytic activity, when the catalyst was used without any regeneration process during the recycle tests. This high catalytic activity and reusability may be ascribed to the well dispersed WO$_x$ species and a strong interaction (synergistic effect) between WO$_x$ and meso-SnO$_2$. This system with a simple WO$_x$/meso-SnO$_2$ catalyst has a remarkable advantage over the desulfurization by more solvent extraction and provides a promising approach for the sulfur removal in the chemical industry.

Conflicts of interest

There are no conflicts to declare.

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Table 2. Rate constant $k$, half-life $t_{1/2}$, and correlation coefficient $R$ of BT, DBT, and 4,6-DMDBT

| Sulfur compound | Rate constant $k$ (min$^{-1}$) | Half-life $t_{1/2}$ (min) | Correlation coefficient $R$ |
|-----------------|-----------------------------|--------------------------|---------------------------|
| DBT            | 0.0631                      | 10                       | 0.9929                    |
| 4,6-DMDBT      | 0.0458                      | 15                       | 0.9903                    |
| BT             | 0.0260                      | 26                       | 0.9951                    |

Fig. 8 (a) Recycle tests of 20 wt% WO$_x$/meso-SnO$_2$ catalyst. Reaction conditions: model oil = 14 mL, acetonitrile = 14 mL, sulfur concentration = 2000 ppm, n[H$_2$O$_2$]: n[S] = 5:1, catalyst = 0.1 g, reaction temperature = 50 °C, time = 60 min. (b) Raman spectra of fresh and spent catalysts.
