Oxidative desulfurization of benzothiophene and thiophene with WO$_x$/ZrO$_2$ catalysts: Effect of calcination temperature of catalysts

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ARTICLE INFO

ABSTRACT

Oxidative desulfurization (ODS) of model fuel containing benzothiophene (BT) or thiophene (Th) has been carried out with WO$_x$/ZrO$_2$ catalyst, which was calcined at various temperatures. Based on the conversion of BT in the model fuel, it can be shown that the optimum calcination temperature of WO$_x$/ZrO$_2$ catalyst is around 700 °C. The most active catalyst is composed of tetragonal zirconia (ZrO$_2$) with well dispersed polyoxotungstate species and it is necessary to minimize the contents of the crystalline WO$_3$ and monoclinic ZrO$_2$ for a high BT conversion. The oxidation rate was interpreted with the first-order kinetics, and it demonstrated the importance of electron density since the kinetic constant for BT was higher than that for Th even though the BT is larger than Th in size. A WO$_x$/ZrO$_2$ catalyst, treated suitably, can be used as a reusable active catalyst in the ODS.

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1. Introduction

Recently, there has been considerable demand to reduce the content of sulfur-containing compounds such as thiophene (Th), benzothiophene (BT), dibenzothiophenes (DBT), and dimethyldibenzothiophenes (DMDBT) in commercial diesel or gasoline to a very low level in order to prevent air pollution from SO$_x$ and catalysts deactivation. For example, based on E.U. and U.S. guidelines, the sulfur level in fuels should be less than 10 and 15 ppmw, respectively [1–3].

Hydrodesulfurization (HDS) has been the most widely used industrial technology for desulfurization for the past several decades [1–5]. However, the process has some shortcomings such as the requirement for high temperature, high pressure and expensive hydrogen, which makes this process costly. Again, side reactions during hydrogenation reduce the octane number [1,5,6]. Moreover, the HDS technique is less effective for removing aromatic thiophenes such as benzothiophene, dibenzothiophene, and their alkyl derivatives [4,5,7] even though it is very effective in removing thiols and sulfides. Additionally, it is not easy to get the sulfur content below 50 ppm with HDS only [6]. Therefore, alternative processes have been sought to overcome these drawbacks.

So far, several processes such as adsorption [6,8–10], biodesulfurization [1,11], and oxidative desulfurization (ODS) [11,12] have been reported in the literature as alternatives or complementary technologies to HDS.

Recently, ODS is drawing significant research interest because of its simple processing and high efficiency [4,13–15]. Generally, the process consists of two steps: the first step is the oxidation of the sulfur compounds with suitable oxidants, whereby these compounds are converted into sulfones and sulfoxides. The next step is the removal of the sulfones and sulfoxides using an appropriate extractive solvent since the chemical and physical properties of sulfones and sulfoxides are notably different from those of the sulfur containing hydrocarbons present in the fuel. Various oxidants such as tert-butyl hydroperoxide [16], hydrogen peroxide (H$_2$O$_2$) [13,14,17], ozone [18], etc. have been used for the oxidation of sulfur compounds. Among them, H$_2$O$_2$ has become a popular and the most widely used oxidant due to its availability and environmentally benign properties [17,19].

In the field of heterogeneous catalysis, ZrO$_2$-based solids are attracting a great deal of attention in recent years. Several ZrO$_2$-based catalysts have been reported so far and WO$_x$/ZrO$_2$ catalysts are highly promising due to their high thermal stability [20,21] and strong acid sites [21,22] along with their significant redox properties [23]. So far, several catalytic reactions with WO$_x$/ZrO$_2$ have been reported. Reactions such as trimerization of isobutene [24], veratrole acylation [21], alkylation of phenols [25,26] and oxidative desulfurization [27–30] have been catalyzed with WO$_x$/ZrO$_2$ catalysts.

As described, ODS with WO$_x$/ZrO$_2$ has been reported by a few groups [27–30]; however, there is no report on the performance of

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WO_x/ZrO_2 calcined at various temperatures for ODS. In this work, we mainly focused on the calcination temperature to find an appropriate and highly active WO_x/ZrO_2 phase, which resulted in high catalytic conversions. As sulfur containing compounds, Th and BT were used since these are the most difficult thiophenic compounds to oxidize according to the mechanism of electrophilic addition of oxygen [31]. The catalysts were characterized with X-ray diffraction (XRD), Raman spectroscopy, and nitrogen adsorption. The effect of the reaction temperature and the kinetics of Th and BT ODS were also investigated in this study.

2. Material and methods

2.1. Materials

All the commercial materials that were purchased for this study were used without further purification. Amorphous WO_x/ZrO_2 (16 wt% WO_3, powder form) was purchased from MEL Corporation. Thiophene (analytical grade, Aldrich) and benzothiophene (analytical grade, Aldrich) were used as the sulfur containing compounds. Acetonitrile (extra pure, Dae Jung chemicals) and *n*-octane (analytical grade, OCI chemicals) were used as extractive solvent and the main component of the model fuel, respectively. Aqueous hydrogen peroxide solution (30 wt% H_2O_2, Junsei chemical) was used as an oxidant.

2.2. Catalyst treatment

To study the influence of calcination temperature on catalytic activity, a 16% WO_x/ZrO_2 catalyst was calcined for 7 h at a temperature within the range of 550–850 °C using a muffle furnace (Thermolyne, US/F48000). The catalysts were represented by WZ-*T* where *T* denotes calcination temperature in °C.

2.3. Characterization

The physicochemical properties of the catalysts were characterized with various analytical techniques. The nitrogen adsorption isotherms were obtained at −196 °C with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation of the obtained samples at 220 °C for 6 h. The surface areas and pore size distributions were calculated with the BET and BJH methods, respectively. XRD patterns of the catalyst were obtained with an X-ray diffractometer (D/MAX-2500, Rigaku). The Raman spectra of the WO_x/ZrO_2 samples were recorded at room temperature with a UV micro Raman spectrometer (Renishaw in via – reflex) in the range of 500–1200 nm. The spectrometer was equipped with a Leica DMLM microscope allowing for confocal measurements. The excitation was done at 514 nm with an argon laser and the size of the laser spot was typically 100 μm.

2.4. Catalytic ODS of the model fuel

Th and BT were dissolved in *n*-octane to prepare a model solution of 1000 ppm of a sulfur-containing compound. The oxidation of the model fuel was done under vigorous stirring using a glass reactor equipped with a condenser. In each run an oil bath, to maintain the reaction temperature, was initially heated and stabilized at the required reaction temperature. Unless otherwise specified, catalytic oxidation was carried out at 60 °C by mixing 10 ml of the model fuel (1000 ppm BT or Th), 20 mg of the catalyst (WZ-700), 0.114 ml and 0.182 ml (for BT and Th) of a 30% aqueous H_2O_2 solution (oxidant to sulfur molar ratio (O/S) = 15), and 5 ml of acetonitrile as an extractive solvent. The resulting mixture was stirred vigorously for a pre-determined time at a constant temperature.
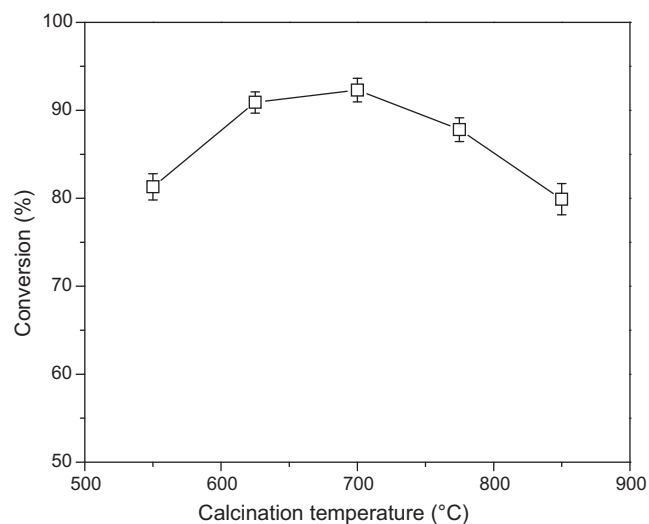
Fig. 1. Effect of calcination temperature of the WO_x/ZrO_2 catalyst on the benzothiophene conversion at 60 °C (catalyst weight: 50 mg; reaction time: 30 min; O/S molar ratio: 15).

After each ODS reaction, samples from the oil phase were withdrawn and analyzed using a GC (DS-6200, DS Science) equipped with a FID. The GC was installed with a HP-1MS capillary column (Agilent, length: 50 m, I.D.: 0.25 mm) and 1,2-dichlorobenzene was used as an external standard. Oxidized products in polar acetonitrile solution were confirmed again with a GC–MS (Agilent, 7890A-5975C GC/MSD).

To investigate the oxidation kinetics and to examine the effects of the various operating parameters on the performances of the ODS process, the oxidation reaction was done at three different temperatures (i.e., 45, 60, and 75 °C). In addition, the ODS reaction was also carried out with different oxidant to sulfur molar ratios (O/S = 5–20).

To study reusability of catalysts, after each ODS experiment, the used catalyst was regenerated in two steps by washing using water–methanol and calcination for 2 h in a muffle furnace at 500 °C. The reusability of a catalyst was studied in two ways. Firstly, the ODS reactions were conducted in a severe condition (reaction temperature: 70 °C; reaction time: 60 min) to accelerate the aging of catalysts. To run an ODS reaction at the very same condition including catalyst weight, several runs were conducted from a fresh catalyst. Secondly, a few experiments were also conducted in a short time (10 min) at 75 °C to find specific rate constants according to the method reported in a literature [32].

3. Results and discussion

3.1. Effect of phases of ZrO_2 and WO_x

Fig. 1 shows the effect of calcination temperature on the desulfurization of BT in the model fuel. The WO_x/ZrO_2 catalysts calcined at five different temperatures show significantly different catalytic activities. The conversion increases with increasing calcination temperatures from 550 °C to 700 °C; however, further increase in calcination temperature results in a decrease of oxidative conversion. Therefore, the catalytic activity can be described in the order of WZ-550 < WZ-625 < WZ-700 > WZ-775 > WZ-850. Hence, it is clear that WZ-700 has the highest catalytic activity in the desulfurization of BT from the model fuel. Complete conversion of 1000 ppm BT is achieved within 30 min of the reaction at 70 °C using 50 mg of the WZ-700 catalyst (see supporting Fig. S1). By comparing the fragmentation patterns of the MS spectrum (m/z = 76, 89, 109, 118,
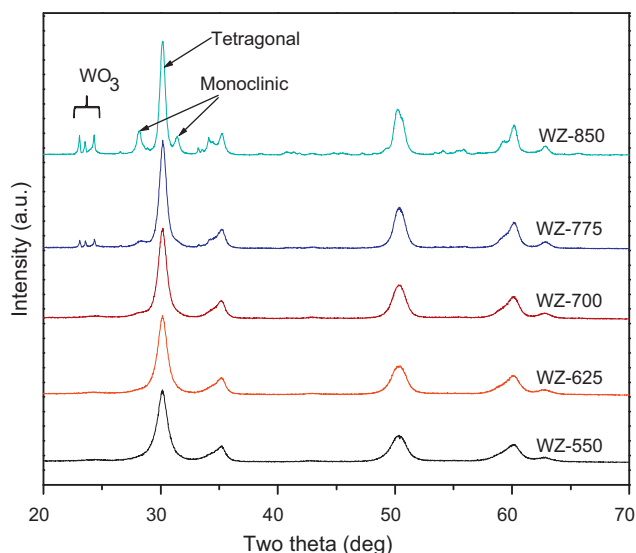
Fig. 2. XRD patterns of the WO$_x$/ZrO$_2$ catalysts calcined at different temperatures.

Fig. 3. Raman spectra of the WO$_x$/ZrO$_2$ catalysts calcined at different temperatures.

137 and 166) with the reported result [33], the oxidized product is confirmed to be benzothiophenedioxide (see supporting Fig. S2). Moreover, the activity is dependent on the catalyst amount and little conversion is observed in the absence of the catalyst (see supporting Fig. S3); therefore, further ODS reaction is studied with the WZ-700 catalyst.

It is not easy to explain the reason why the WZ-700 shows the best performance among the catalysts even though it has been reported that the calcination temperature has a significant effect on the catalytic activity of WO$_x$/ZrO$_2$ catalysts in an acid catalysis [24]. Hence, the physicochemical properties of the catalysts were analyzed with several characterization methods. Fig. 2 shows the XRD patterns of the amorphous and calcined WO$_x$/ZrO$_2$ catalysts. Up to the calcination temperature of 700 °C, only tetragonal ZrO$_2$ phases are observed. Moreover, the concentration of the pure tetragonal ZrO$_2$ phases is the highest for WZ-700, which is in good agreement with previous reports [24,25]. As the calcination temperature increases up to 775 °C, monoclinic ZrO$_2$ and crystalline WO$_3$ [24,25] gradually appear. Moreover, the intensity of monoclinic ZrO$_2$ and crystalline WO$_3$ increases with an increase in calcination temperature up to 850 °C. Nevertheless, the surface area of the WO$_x$/ZrO$_2$ catalysts gradually decreases with increasing calcination temperature (Table 1 and supporting Fig. S4). Therefore, it can be assumed that the tetragonal rather than monoclinic phase is beneficial for the good performance of the catalysts for ODS.

Fig. 3 shows the Raman spectra of the WO$_x$/ZrO$_2$ samples calcined at different temperatures. The band at 646 cm^{-1} can be assigned to the tetragonal phase of ZrO$_2$ [34]. On the other hand, monoclinic ZrO$_2$ phase can be identified from the bands at 560 cm^{-1} and 617 cm^{-1} [34]. Therefore, from Fig. 3, it is clear that the monoclinic ZrO$_2$ phase gradually appears when the calcination temperature is above 775 °C. The samples calcined up to 700 °C
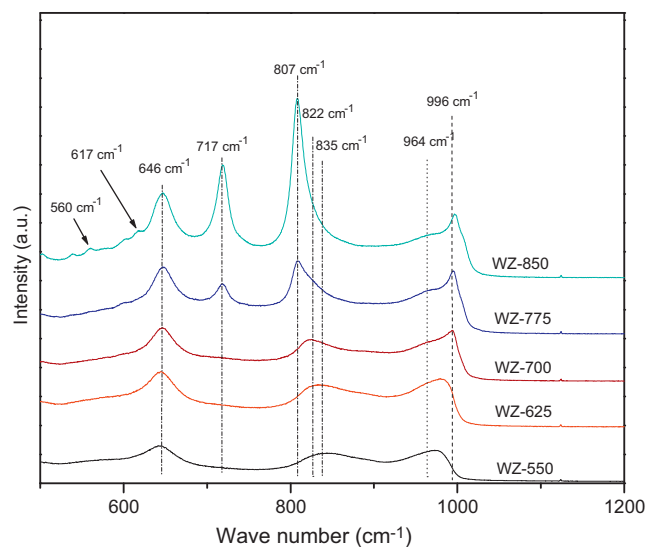
have a band at around 822 cm^{-1}, attributed to W–O–W stretching modes, as well as two higher frequency bands at 964 cm^{-1} and 996 cm^{-1}, assigned to W=O stretching modes, that indicates the presence of hydrated interconnecting polyoxotungstate clusters [35,36]. With further increase in calcinations temperature, two new bands at about 716 cm^{-1} and 807 cm^{-1} are observed which may be assigned to W–O–W and W=O stretching modes, respectively, in microcrystalline WO$_3$ species [35,36]. Torres-García et al. [28] also reported that these two bands (716 cm^{-1} and 807 cm^{-1}) arise from the crystalline domains of WO$_x$ when the calcination temperature is 800 °C (WO$_x$/ZrO$_2$, loaded with > 15% W) which is in good agreement with our results. It is also observed that the W=O stretching band at 996 cm^{-1} shifted to higher frequency with the increase of calcination temperature above 700 °C. This may be due to the condensation of surface polyoxotungstate species to microcrystalline WO$_3$ that ultimately resulted in the lower W dispersion over ZrO$_2$ [37]. It is also noticed that the sample calcined at lower temperature (550 °C) showed band for W=O vibration corresponding to tetrahedral W^{6+} at 834 cm^{-1} [32,38]. However, with the increase of calcination temperature this band became insignificant. Therefore, considering poor activity of WZ-550 in this study, the role of tetrahedral W species [32] may not be very important in ODS.

Moreover, it is reported that WO$_3$ crystallites in WO$_x$-ZrO$_2$ materials are usually observed after saturation of the zirconia surface by tungsten species [35]. Therefore, the samples calcined above 700 °C, the monolayer coverage was largely surpassed which is revealed by the high intensity of the Raman bands at 716 cm^{-1} and 807 cm^{-1} associated with crystalline WO$_3$ species. Moreover, there is possibility that these surface species may lose their effectiveness at high temperatures because they diffuse into the bulk and decompose/agglomerate to form WO$_3$ crystalline phase [39]. Therefore, our results which include ODS and catalysts characterizations with XRD and Raman show that a highly dispersed polyoxotungstate species [35,36,40,41] have higher ODS activity than poorly dispersed crystalline WO$_3$.

3.2. Kinetics of Th and BT oxidation

Considering 700 °C as the optimum calcination temperature, further experiments were done with WZ-700 catalyst under various conditions to shed light on WO$_x$/ZrO$_2$ as a potential catalyst in the desulfurization of Th and BT from model fuel. The oxidation reaction of Th and BT was also done with various O/S molar ratios

Table 1
Specifications of the WO$_x$/ZrO$_2$ catalysts.

Sample	Calcination temperature (°C)	BET Surface area (m^2/g)
WZ-amorphous	Without calcination	270
WZ-550	550	136
WZ-625	625	109
WZ-700	700	91
WZ-775	775	76
WZ-850	850	49

Table 2
Pseudo-first-order rate constants and correlation factors of the benzothiophene oxidation over WZ-700 catalyst at different temperatures.

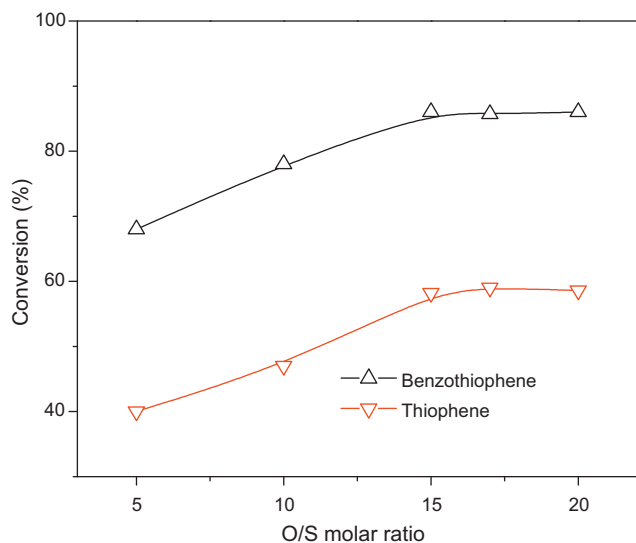| Temperature (°C)	Thiophene		Benzothiophene	
	Rate constant k (min^{-1})	Correlation factor R^2	Rate constant k (min^{-1})	Correlation factor R^2
45	7.0×10^{-3}	0.98	1.8×10^{-2}	0.98
60	1.5×10^{-2}	0.99	2.8×10^{-2}	0.99
75	2.3×10^{-2}	0.98	3.9×10^{-2}	0.98

at 60 °C in order to investigate the effect of the amount of the oxidant on the oxidation activity. As shown in Fig. 4, when the O/S ratio increases from 5:1 to 15:1, BT conversion increases from 68% to 86%; and Th conversion increases from 40% to 59%. The oxidation activity of the catalyst for Th and BT increases with the O/S molar ratio up to O/S = 15, and remains almost constant with any further increase in the O/S molar ratio. It is noteworthy that the optimum value of the O/S molar ratio is much higher than the stoichiometric O/S molar ratio required to oxidize Th or BT. The requirement for excess oxidant may be due to side reactions including thermal decomposition of H_2O_2 [42].

To understand ODS kinetics, the oxidation of Th and BT was studied at three different temperatures (45, 60, and 75 °C) and the results are shown in Fig. 5(a) and (b), respectively. An increase in the reaction temperature from 45 to 75 °C leads to a remarkable removal of Th and BT from 53 to 65% in 3 h and from 65 to 91% in 2 h, respectively. The increase in the conversion with increasing reaction temperatures is in good agreement with previous reports [13,42].

The experimental data were fitted to a pseudo-first-order rate equation Eq. (1).

$$\ln \left(\frac{C_t}{C_0} \right) = -kt \tag{1}$$

Here, k is the rate constant; C_0 (ppm) and C_t (ppm) are the concentrations of sulfur containing compounds (Th or BT) at time 0 min and t min, respectively. As shown in Fig. 6, plots of $\ln(C_t/C_0)$ versus reaction time (t) display linear relationships, confirming the pseudo-first-order reaction kinetics of ODS in the present conditions. From Table 2, it is clear that the rate constant increases with an increase in the reaction temperature for both Th and BT. Moreover, at the temperatures investigated, the rate constants for BT are higher than those for Th, which can be explained by the fact that the oxidation of BT is easier than that of Th. The dependence of the rate constant k on the reaction temperature can be expressed with the Arrhenius equation (Eq. (2)):

$$k = Ae^{-(E_a/RT)} \tag{2}$$

where A is the pre-exponential factor; E_a is the apparent activation energy; and R and T are the gas constant and reaction temperature (K), respectively. The Arrhenius plots are shown in Fig. 7 and the calculated E_a values for the oxidation of Th and BT are 36.6 kJ/mol and 23.5 kJ/mol, respectively. Therefore, the E_a for BT is less than that for Th, and this result can be easily explained with the concept of electrophilic addition of oxygen or the high electron density on S of BT. Since the electron density on S of BT (5.739) is higher than that of Th (5.696) [31], oxidation of BT is easier than that of Th, as observed in this study. The high activity of BT, compared with Th, was also reported for ODS with MoO_3 catalysts [14]. However,
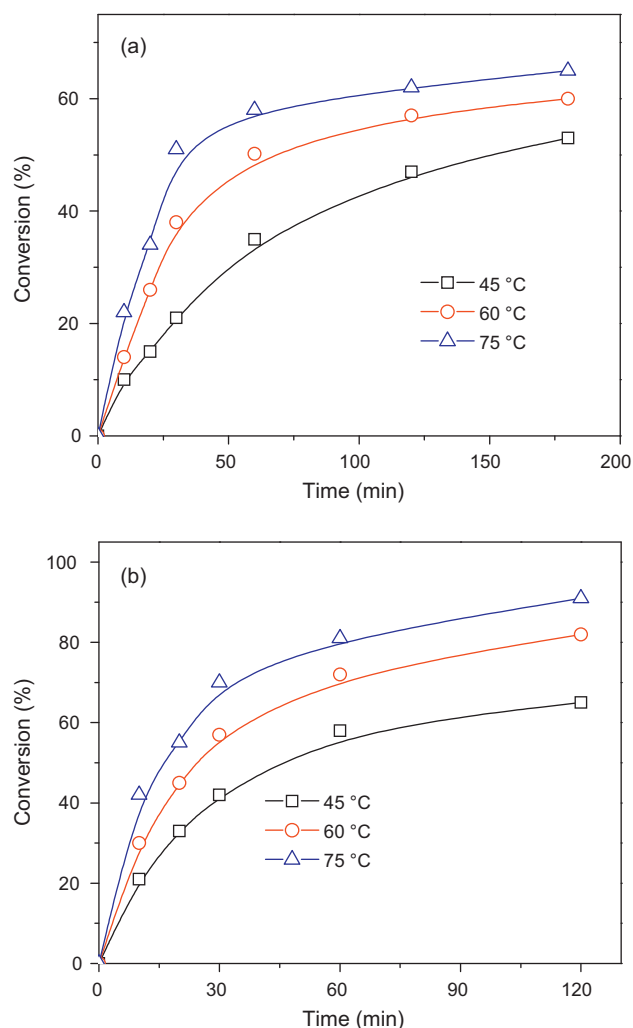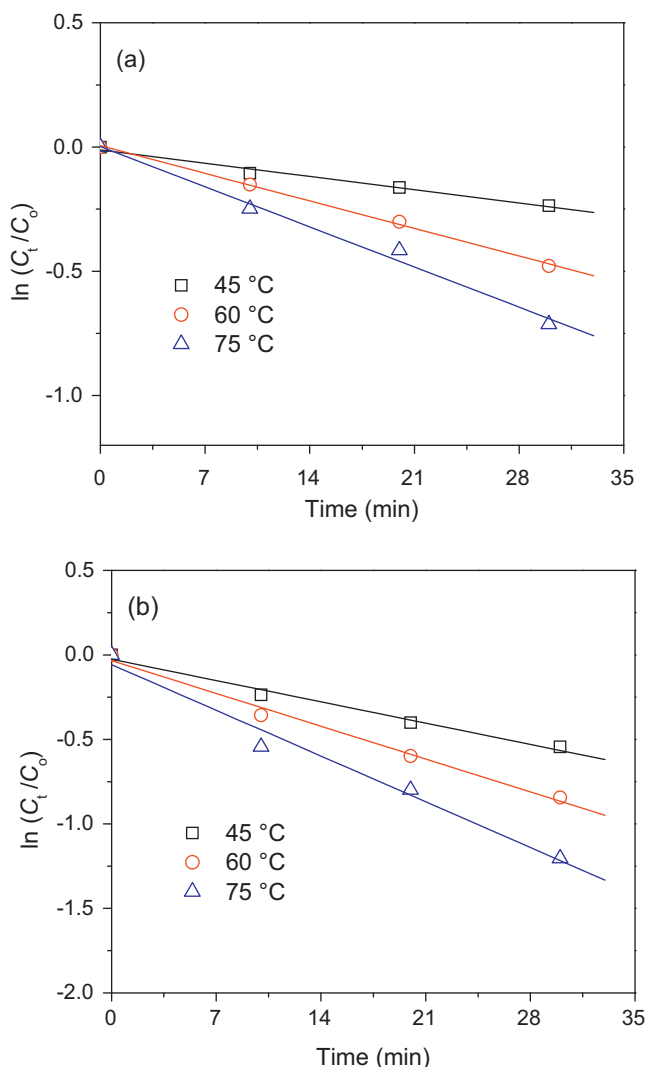

Fig. 4. Effects of O/S molar ratio on the conversions of thiophene and benzothiophene (catalyst weight: 50 mg of the WZ-700; reaction time: 30 and 20 min for thiophene and benzothiophene, respectively).


Fig. 5. Effect of reaction temperature and time on the conversion of (a) thiophene and (b) benzothiophene with the WZ-700 at 45, 60 and 75 °C.

Fig. 6. Plots of the pseudo-first-order kinetics for the oxidation of (a) thiophene and (b) benzothiophene at 45, 60 and 75 °C with WZ-700 catalyst.
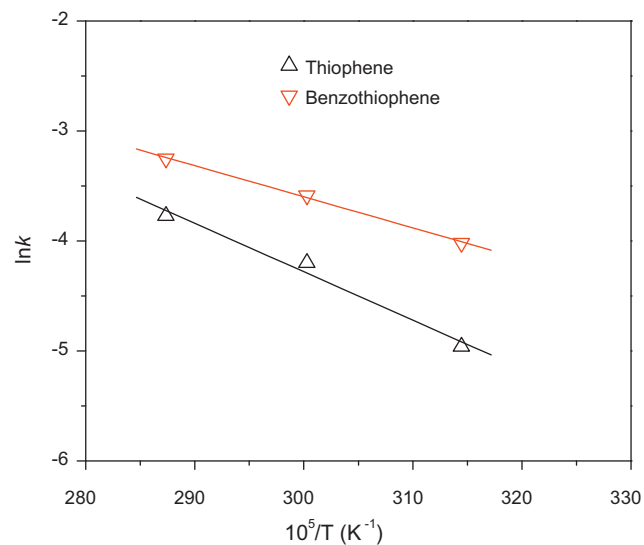
Fig. 7. Arrhenius plots to get the activation energies for the oxidation of thiophene and benzothiophene with the WZ-700 catalyst.
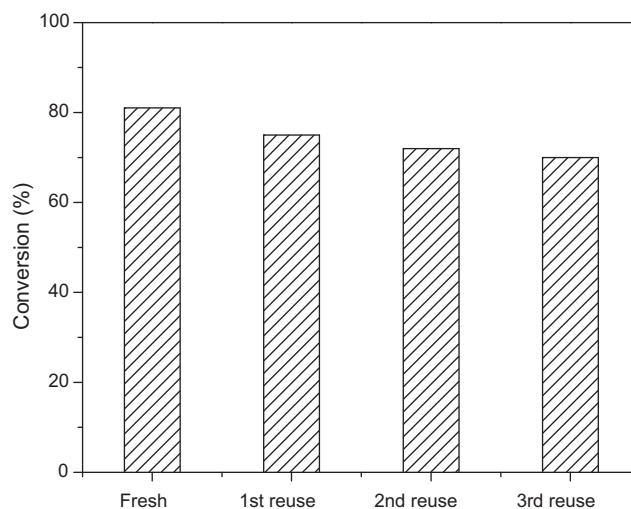
Fig. 8. Conversion of BT with the fresh and reused WZ-700 catalysts (catalyst weight: 20 mg; reaction time: 60 min; reaction temperature: 70 °C).

the activity was in the order of Th > BT for ODS with a microporous catalyst Cu/TS-1, probably due to a hindered diffusion of BT in the microporous catalysts [43]. On the contrary, WZ-700 is a mesoporous catalyst (supporting Fig. S5), and therefore, there is little diffusive hindrance even for the comparatively bulky BT.

3.3. Reusability of catalyst

The reusability of a catalyst is very important for commercial feasibility. The XRD pattern (supporting Fig. S6) shows that the WZ-700 retains its structure after the ODS reaction. Moreover, the reusability of the WZ-700 catalyst for the ODS of BT has been investigated for several runs after simple washing and calcination. Even though the activity decreases slightly with increasing numbers of recycling of the catalyst, the activity after the third recycle is not so low compared to a fresh catalyst (Fig. 8). Additionally, the kinetic constants of reactions for 10 min at 75 °C were quite stable even in second reuse (k_{fresh} = 2.10 min^{-1} g^{-1}; $k_{first\ reuse}$ = 2.06 min^{-1} g^{-1}; $k_{second\ reuse}$ = 2.05 min^{-1} g^{-1}). Complete conversion of BT within 30 min for a selected condition (supporting Fig. S1) and reusability of the catalyst suggest that WZ-700 is a potential catalyst which can be applied in ODS reactions.

4. Conclusion

The following conclusions can be derived from the ODS of BT and Th with WO$_x$/ZrO$_2$ catalysts that have been calcined at various temperatures. The most active WO$_x$/ZrO$_2$ catalyst is composed of tetragonal zirconia (ZrO$_2$), with well dispersed polyoxotungstate species, with minimum content of crystalline WO$_3$ and monoclinic ZrO$_2$. The optimum calcination temperature is around 700 °C for an active ODS catalyst even though the porosity of the WO$_x$/ZrO$_2$ catalyst is low compared with catalysts calcined at lower temperatures. The ODS for BT and Th shows that a high electron density on sulfur is important to increase the oxidation rate since the kinetic constant for BT is higher than that for Th. The activation energy also shows that ODS for BT is easier than ODS for Th. The WO$_x$/ZrO$_2$ catalyst may be applied to ODS of commercial fuels if it is calcined at suitable conditions because of its easy synthesis, reusability and high activity.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.059.

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