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A new simple protocol for the synthesis of nanohybrid catalyst for oxidative desulfurization of dibenzothiophene

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Abstract

This study offers an investigation of the catalytic activity of TiO₂/SiO₂ during oxidative desulfurization (ODS) of a model fuel that includes dibenzothiophene (DBT), using hydrogen peroxide (H₂O₂) as a green oxidant in the absence of UV irradiation. For the first time, though a novel and simple protocol, TiO₂/SiO₂ nanohybrid was synthesized using ascorbic acid and glycerol as green complexing and polymerizing agents, respectively. The TiO₂/SiO₂ catalyst was thoroughly characterized by XRD, FT-IR, nitrogen adsorption-desorption measurements, TEM, FESEM, and TGA. Results revealed a high catalytic oxidative activity for the catalyst in the removal of DBT regarding sulfur removal up to 99.4% within 20 min under optimum reaction conditions. The main factors affecting the ODS process, including catalyst dosage, temperature, O/S molar ratio, and different oxidizing agents, were evaluated to identify optimum conditions. The desulfurization efficiency of the recoverable catalysts showed no loss in activity after four times. The present article suggests a new and green method for the synthesis and characterization of an efficient catalyst (TiO₂/SiO₂) in deep oxidative desulfurization at 25 °C and removal of refractory organosulfur compounds that yield ultra-low sulfur fuels. Also, it proved to have a much higher catalytic oxidation capacity when compared to pure TiO₂.

Keywords Oxidative desulfurization · Catalyst · TiO₂/SiO₂ · Dibenzothiophene

Introduction

During the combustion of fossil fuels, sulfur-containing compounds convert to SO_x which is the main cause of air pollution and health problems and leads to the formation of acid rains (Kabala, 1989; Bascom et al., 1996). In particular, thiophene compounds in the fuels are bound to damage the exhaust catalytic converters in vehicles, resulting in the emission of carbon monoxide, nitrogen oxides, and hydrocarbons with incomplete combustion, which have a detrimental effect on the environment (Miao et al., 2015). Also, existing sulfur in the diesel can poison the fuel-cell electrodes and decline their efficiency to a

large extent (Shen et al., 2016; Qin et al., 2018). Meanwhile, under the stringent environmental regulations, a maximum level of sulfur in fuels was set as 10 ppm (2009) and 15 ppm by the European Union (EU) legislation and US Environmental Protection Agency (EPA), respectively (Pawelec et al., 2011; Stanislaus et al., 2010; Kulkarni and Afonso, 2010). As a result, many researchers have been focused on developing ultra-deep desulfurization technologies to prevent and reduce environmental impacts. Hydrodesulfurization (HDS) as one of the most widely used desulfurization technologies operates at high temperatures (> 300 °C) and high pressures of H₂ (20–100 MPa) in the presence of Al₂O₃ supported Ni–Mo or Co–Mo sulfide catalyst (Wang and Yang, 2007; Hernández-Maldonado et al., 2005). Also, HDS is effective in removing mercaptans, sulfides, and disulfides from fossil fuels, but difficult, costly, and not efficient to elimination refractory compounds such as benzothiophene (BT), dibenzothiophene (DBT), and their derivatives (Javadli and De Klerk, 2012; Ahmadpour et al., 2019). Also, more stringent pressure and temperature, as well as higher hydrogen consumption, are required to produce ultra-low sulfur fuels through HDS (Abro et al., 2016; Röthlisberger and Prins, 2005; Zhang et al., 2013; Wang et al., 2010b; Zarrabi et al., 2015; Guo et al., 2019). The reason is usually attributed to the

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low hydrogenation reactivity of the thiophenic compounds, which is caused by the steric hindrance effect (Li et al., 2016b). Hydrodesulfurization is also likely to reduce the octane number of gasoline (Hou et al., 2017), which is considered as another drawback. Hence, it is worth seeking and developing alternative approaches such as biodesulfurization (Davoodi-Dehaghani et al., 2010; Bhasarkar et al., 2015a, b), selective adsorption (Xiong et al., 2015; Tian et al., 2014), oxidative desulfurization (ODS), extraction desulfurization (Li et al., 2016c), sono-hybrid (Li et al., 2016b; Bhasarkar et al., 2015a, b) technique, and also alkylation to overcome HDS disadvantages. Due to the ability of ODS to deeply removal of refractory organosulfur compounds in fuels under mild operating conditions without using costly hydrogen, it has drawn significant attention and recognized as a promising alternative technique for ultra-deep desulfurization (Bhadra et al., 2017; Wang et al., 2010a; Piscopo et al., 2018; Gao et al., 2010; Wang et al., 2017; Kim et al., 2012; Thornburg and Notestein, 2017; Abdelrahman et al., 2018; Alhadhami et al., 2017). ODS usually consists of two steps: oxidation of sulfur-containing compounds into their corresponding sulfones and sulfoxides by suitable oxidants over an appropriate catalyst and, subsequently, removal of oxidized products using polar solvent extraction (Zhu et al., 2015). Hydrogen peroxide (cheap, environmentally friendly, commercially available), organic peroxides, ozone, air, molecular oxygen, etc. are usually used as the oxidant in ODS (Zhang et al., 2013; Bhadra et al., 2017). A wide variety of catalysts have also been reported in the literature for oxidative desulfurization of liquid fuels, such as polyoxometalates (Wang et al., 2010b) and their composites (Wang et al., 2010a; Zhu et al., 2015), supported metal oxides (Shen et al., 2016; Bhadra et al., 2017), phase transfer catalysts (Jiang et al., 2009; Zhang et al., 2010), titanate nanotubes (Lorençon et al., 2014), and so on. Facile preparation, low cost, good efficiency, and convenient recyclability are considered as important parameters for an appropriate catalyst. Besides, no ODS process has been described in a commercial scale (Bhadra et al., 2017). Therefore, it is still required to develop and evaluate new catalysts for oxidative desulfurization. In this respect, the use of TiO₂-based materials as catalyst, photocatalyst, or an adsorbent has been widely investigated in oxidative desulfurization owing to high activity, chemical stability, non-toxicity, and inexpensiveness (Shen et al., 2016; Li et al., 2018). Nano-TiO₂ was reported by Wang et al. (2012) to exhibit high photocatalytic activity for removal of DBT (98.2%) after 10 h of UV irradiation. Wang et al. (2014) found that the removal of DBT could reach 98.9% using TiO₂ loaded on C₃N₄ as the photocatalyst under optimized conditions after 2 h. Zhu et al. (2014) studied the photocatalytic activity of different forms of TiO₂ in desulfurization and found that adding hydrogen peroxide improves the catalytic activity of TiO₂ powder. The authors also revealed that the removal of DBT in model oil reaches 96.6% with amorphous TiO₂, which was more effective than a system with

anatase TiO₂ (23.6%) or with anatase-rutile TiO₂ (18.2%). Furthermore, TiO₂/SiO₂ was employed by Miao et al. (2015) as both a photocatalyst (to oxidize thiophenic compounds) and meanwhile an adsorbent (to selectively adsorb the oxidized thiophenic compounds) for photocatalytic-adsorptive desulfurization of model fuel under UV irradiation. The results showed that the organosulfur uptake could reach to 5.12 mg/g on the optimized 0.3TiO₂/0.7SiO₂ adsorbent after 7 h at a low sulfur concentration of 15 ppm, and its adsorption selectivity over naphthalene was up to 325.5. However, the efficiency of photocatalytic-adsorptive desulfurization with TiO₂/SiO₂ is not high enough, and the system is needed to be much more improved.

Although some researchers have been conducted the adsorptive or photocatalytic-adsorptive activity of TiO₂/SiO₂ in desulfurization (Miao et al., 2015; Qin et al., 2018; Li et al., 2018; Xu et al., 2016), little information on the use of TiO₂/SiO₂ as a catalyst in oxidative desulfurization is available. The purpose of this study is to propose a novel, simple, and safe method for the synthesis of TiO₂/SiO₂ substrate and the study of its catalytic activity in deep oxidative desulfurization of a model fuel containing DBT without UV irradiation. The catalyst was characterized using various techniques. The main factors affecting the process were systematically examined to find optimum conditions for the oxidative desulfurization of the model fuel. Moreover, a proposed mechanism was presented to investigate the oxidation process of DBT with TiO₂/SiO₂ catalyst in the presence of hydrogen peroxide as a green oxidizing agent.

Experimental

Materials

The chemicals and reagents were used without further purification. Dibenzothiophene (DBT, 98%), n-octane (99%), acetonitrile (99.9%), hydrogen peroxide (aqueous solution, 30%), tert-Butyl hydroperoxide solution (aqueous solution, 70%), NaIO₄ (purity > 99%), tetraethyl orthosilicate (purity >99%), titanium (III) chloride, L-ascorbic acid (purity > 99%), and glycerol were purchased from Sigma Company. Deionized (DI) water (18.3 MΩ cm) was used throughout the research.

Instruments

The X-ray diffraction (XRD) spectra were obtained by a Bruker D8 advance X-ray diffractometer with Cu Kα (1.54178 Å) radiation. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ using Thermo Nicolet system. The analysis of thermogravimetric was done using Shimadzu-50. To examine the morphology of samples, field emission

Table 1 Molar quantities of materials used in the synthesis of titania-silica nanohybrids (TiO₂/SiO₂)

Sample	TiO ₂ /SiO ₂ (molar ratio)	TiCl ₃ (mol)	TEOS (mol)	Glycerol (mol)	Ascorbic acid (mol)
T	100/0	0.025	-	0.05	0.1
TS-1	90/10	0.9	0.1	3.6	7.2
TS-2	80/20	0.8	0.2	3.2	6.4
TS-4	60/40	0.6	0.4	2.4	4.8

scanning electron microscopes (FESEM, MIRA III) and transmission electron microscopy (TEM, Philips cm 120) were employed. To determine the specific surface area, pore diameter, and total pore volume of samples, nitrogen adsorption/desorption isotherms were used according to the Brunauer-Emmett-Teller (BET) method. UV-Vis spectrophotometer (SPEKOL 1300) was applied to monitor the progress of the reaction. The absorption of DBT was monitored with a UV-Vis spectrophotometer at $\lambda_{\text{max}} = 325$ nm. To analyze the sulfur content of samples, a gas chromatography (Agilent-6890) equipped with an FID and HP-5 ms capillary column was employed. The following conditions were used for the analysis of DBT in GC analysis: injection volume of 1 μL ; pure nitrogen as a carrier gas; column flow = 1.9 mL/min; temperature of injection port = 280 °C; temperature of detector = 320 °C; and oven temperature program = 170 °C held for 2 min and then 170–250 °C at a 10 °C/min gradient, held for 5 min. Also, gas chromatography-mass spectrometry (GC-MS) was used to identify the oxidation products of DBT by the use of Thermoquest-Finnigan Trace GC-MS instrument.

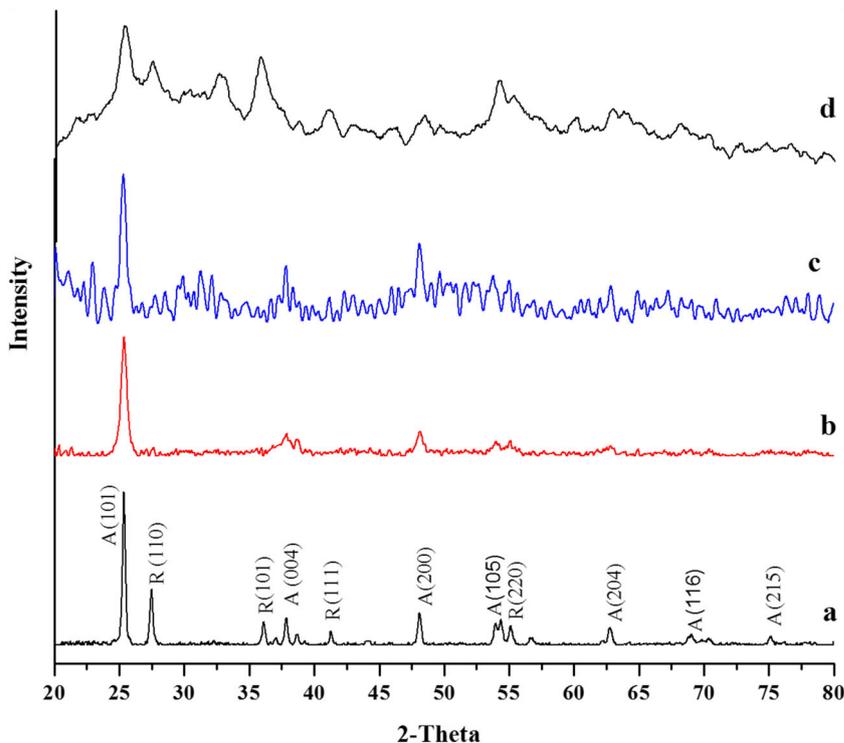
Preparation of TiO₂ nanoparticles

In a typical procedure, 0.025 mol of TiCl₃ is added to the solution resulted from the dissolution of 0.1 mol ascorbic acid in water and stirred for 5 min at 25 °C. Afterward, 0.05 mol of glycerol is slowly added to the resulting solution and then refluxed at 100 °C for 2 h. After the reflux, the solution is subjected to indirect heat at 80 °C for 4 h to obtain a viscose gel, which is then heated directly to turn to dried gel. Afterward, the dried gel was ground and calcinated at 600 °C for 5 h, and finally, titanium oxide nanoparticles were prepared.

Synthesis of TiO₂/SiO₂ nanohybrids

In the synthesis method, the initial solution contains ascorbic acid as a complexing agent to prevent the formation of large clusters and particles agglomeration and glycerol as a polymerizing agent for the homogeneous particle size distribution.

Fig. 1 X-ray diffraction pattern of TiO₂/SiO₂ (from a to d increase in the silica mole percent; 0%, 10%, 20%, 40%, respectively); A = anatase, R = rutile



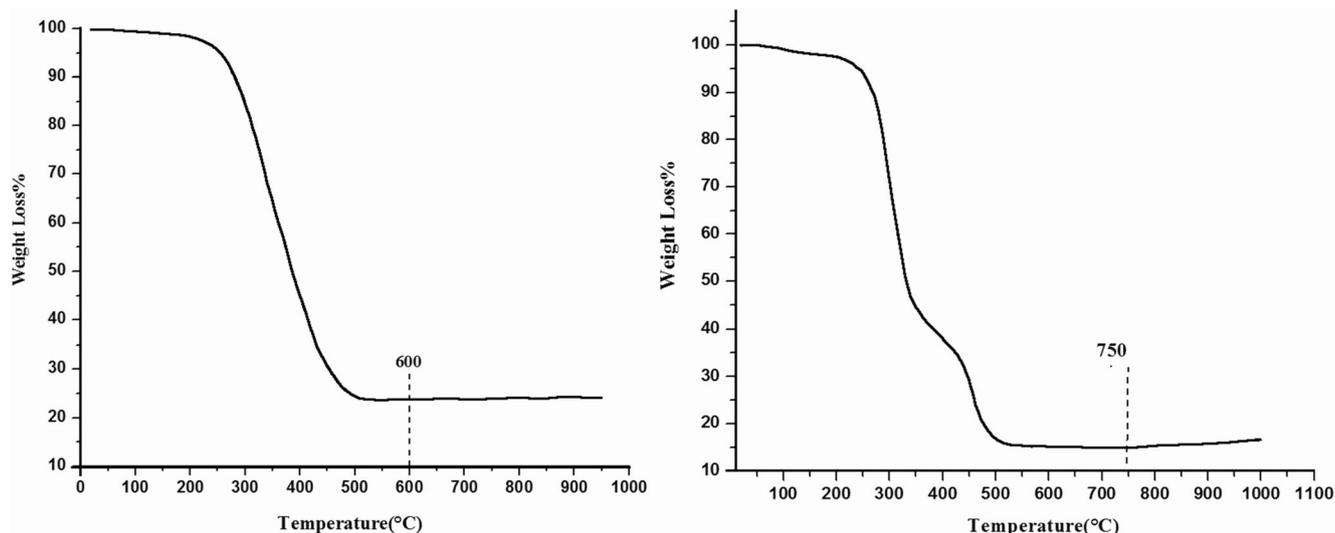


Fig. 2 The TGA curve for the synthesis of TiO₂, TS-1, TS-2 (left), and TS-4 (right)

To study the effect of different silica loading on the structural properties, specific surface area, and catalytic activity, titania-silica nano hybrids were prepared with various molar ratios of TiO₂/SiO₂ as given in Table 1.

To prepare each molar ratio of TiO₂/SiO₂, a certain amount of titanium (III) chloride and tetraethyl orthosilicate was dissolved in a beaker containing distilled water. Afterward, glycerol and ascorbic acid were added at regular intervals. The resulting mixture was stirred at 25 °C for 15 min until a completely clear solution was obtained (the solution color is clear violet). The solution was refluxed at 100 °C for 1 h which turned into metal-ascorbic homogeneous complex. The reflux process not only increases the solubility of ions in the solution but also leads to complex formation between ascorbic acid and metal cations. The complex formation is completed in the

mild-heating phase, which then bundled together in the polymerization step. In the reflux step, the solution evaporates repeatedly and cools in a condense and returns to the boiling flask. By repeating this process, a homogeneous solution is prepared. It should be noted that the solution volume at this step should not noticeably be reduced. The initial volume is 60 cm³; after the reflux, it should be between 55 and 60 cm³. Interaction between the hydroxyl groups of ascorbic acid with titanium and silicium cations prevents the growth and accumulation of particles. After reflux, the volume of the solution does not change, but its color becomes slightly more intense (the solution color is black violet), resulting from concentration increase and the formation of complexes. Then, the solution is heated mildly at 80 °C in an oil bath. At this step, a wet viscose gel is formed. At the direct heating stage, the container was removed from the oil bath and placed directly on the hot plate. When the solvent is completely evaporated, the gel is slowly bloated and then gradually dried, and its color turned to dark brown, which is converted to black by the increase of the heating time. Afterward, the dried gel is well crushed and ground in the mortar, and the resulting powder is then calcined at a *convenient*

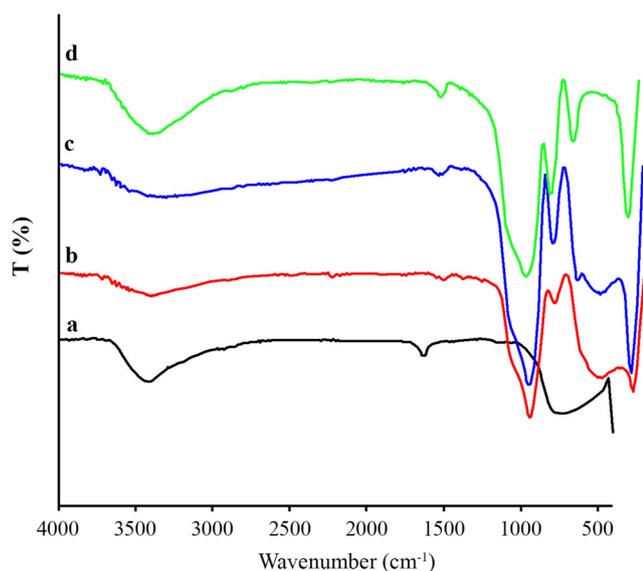


Fig. 3 FT-IR spectra of (a) pure TiO₂, (b) TS-1, (c) TS-2, and (d) TS-4

Table 2 Properties of TiO₂ and nano hybrids with different molar ratios of TiO₂/ SiO₂

Catalyst samples	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
T	23.4	0.232	39.19
TS-1	28.6	0.200	27.92
TS-2	154.0	0.879	22.82
TS-4	224.5	1.092	19.45

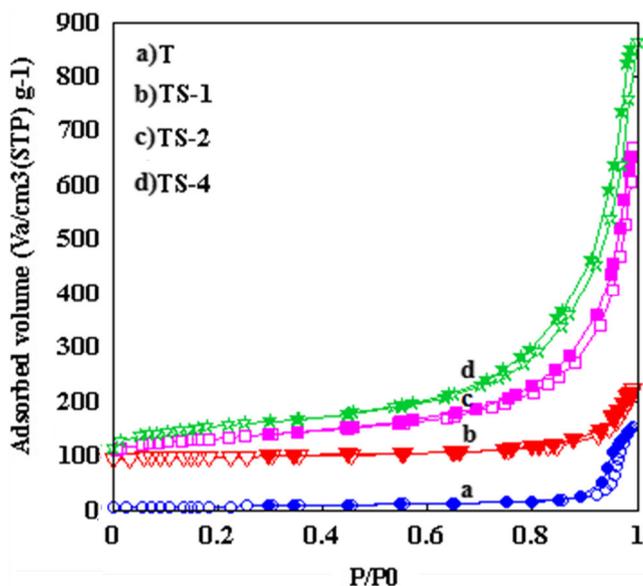


Fig. 4 Nitrogen adsorption/desorption isotherms of (a) TiO₂, (b) TS-1, (c) TS-2, and (d) TS-4

temperature for 5 h. Finally, the white titanium-silica oxide nanohybrids are prepared.

General procedure for desulfurization of the model fuel

In general, the amount of catalyst was added to a solution of hydrogen peroxide and 5 mL of acetonitrile. The process was started by further addition of a solution of 500 ppm DBT in octane (5 mL) to the above mixture under stirring. After a certain time, the upper clear solution (n-octane phase) was withdrawn from the reaction mixture. Progress in desulfurization was monitored by UV-Vis spectroscopy and GC. Also, the oxidation product of DBT was recognized via gas chromatography-mass spectrometry (GC-MS).

Fig. 5 TEM images of the TS-4 nanohybrids (a) and SEM image of TS-4 nanohybrids (b)

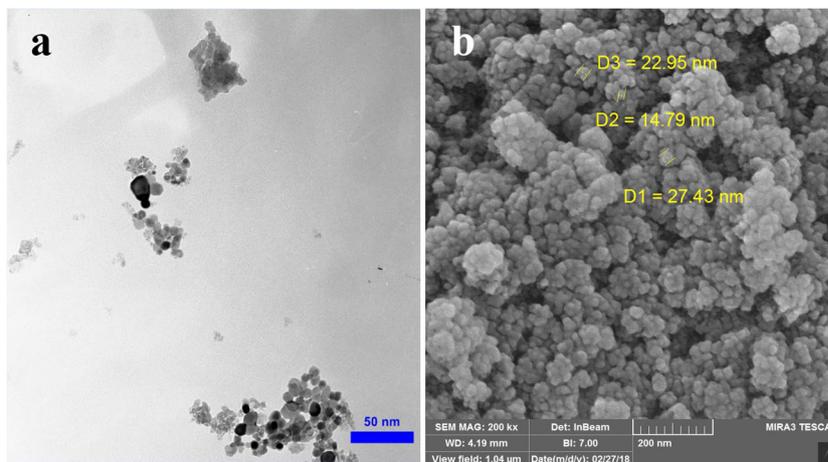


Table 3 Comparison of catalytic performance of TiO₂/SiO₂ catalysts with different molar ratios of SiO₂ on DBT removal

Entry	Catalyst	DBT removal (%) ^a	
		Catal + H ₂ O ₂ + solvent ^c	Catal + H ₂ O ₂
1	T	71	3.5
2	TS-1	84	3.6
3	TS-2	90.1	4.2
4	TS-4	99.4	4.9

^a Reaction conditions: T = 25 °C, O/S = 10, catalyst dosage = 0.03 g, t = 30 min, initial sulfur content = 500 ppm

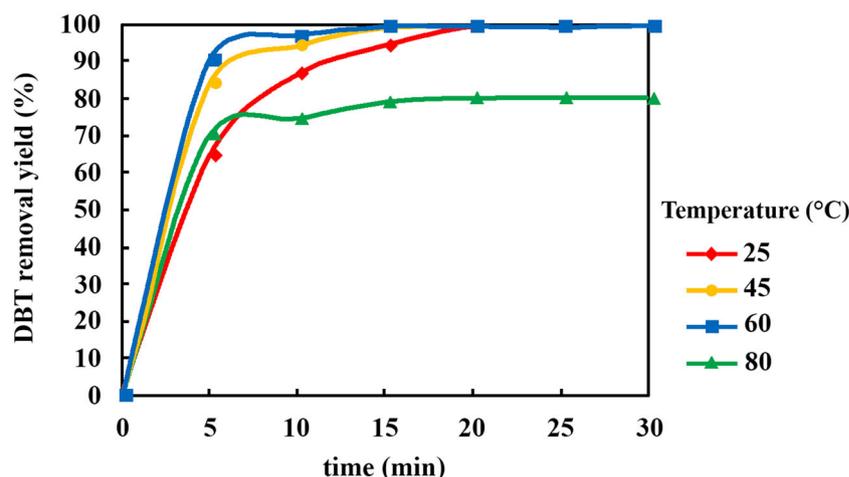
^c solvent: Acetonitrile

Results and discussion

Fabrication and characterization of the catalyst

At the first step of this study, TiO₂/SiO₂ nanohybrids were prepared with various TiO₂/SiO₂ molar ratios with diameters of approximately 3–9 nm through the polymerizing-complexing (PC) sol-gel method (refer back to Sect. 2.4). The spectral and analytical data confirmed the successful synthesis of the mentioned nanocatalyst. The X-ray diffraction spectra of TiO₂/SiO₂ samples with different molar ratios are shown in Fig. 1. The distinctive diffraction peaks appeared (Fig. 1a) at 2θ of 25, 38, 48, 54, 55, 63, 69, 70, and 75 are respectively the characteristics of (101), (004), (200), (105), (211), (204), (116), (220), and (215) reflection planes of tetragonal crystal of anatase TiO₂ (JCPDS No. 21-1272) (Jafarpour et al., 2015; Peng et al., 2010). The other diffraction peaks observed at 2θ of 27, 35, 41, and 56 were assigned to the (110), (101), (111), and (220) reflection planes of the tetragonal crystal of rutile TiO₂, respectively (JCPDS No. 21-1276) (Jafarpour et al., 2015; Ye et al., 2008). The results obtained from XRD patterns (Fig. 1 b–d) disclosed that increment in the molar portion of SiO₂ leads to the width increase

Fig. 6 Effect of temperature on the DBT oxidative removal. Reaction conditions: O/S = 10, initial sulfur content = 500 ppm, and dosage catalyst = 0.03 g



of the diffraction peaks and the decrease in their intensity. This arises from the incorporation of amorphous silica within the nanohybrid structure as well as decreasing the size of the nanocrystallites. It is also noteworthy that the most crystallites size is for the (101) crystalline direction, which is related to the presence of the anatase phase in the nanohybrids.

The thermogravimetric analysis (TGA) of amorphous powder dried at 120 °C was carried out from 25 °C to 1000 °C. Accordingly, TGA analysis of the crushed powder was carried out to fix the calcination temperature for the production of TiO₂/SiO₂ nanohybrids. As-prepared crushed powders were annealed at 600, 600, 750, and 600 °C for the synthesis of TS-1, TS-2, TS-4, and TiO₂ nanopowders, respectively (Fig. 2).

The FT-IR spectra of four nanohybrids with different molar ratios are shown in Fig. 3. The peaks appeared in the region of 1635 cm⁻¹ and 3426 cm⁻¹ correspond to hydroxyl groups. The presence of peaks at 802 cm⁻¹ and 1103 cm⁻¹ is related to the symmetric and asymmetric vibrations of the Si-O-Si group, respectively (Kannaiyan et al., 2010). The peak located at 950 cm⁻¹ is attributed to the vibration of Si-O-Ti group and the peak located in the region of 610–450 cm⁻¹ ascribed to the stretching vibration of the Ti-O group (Pakdel et al., 2013;

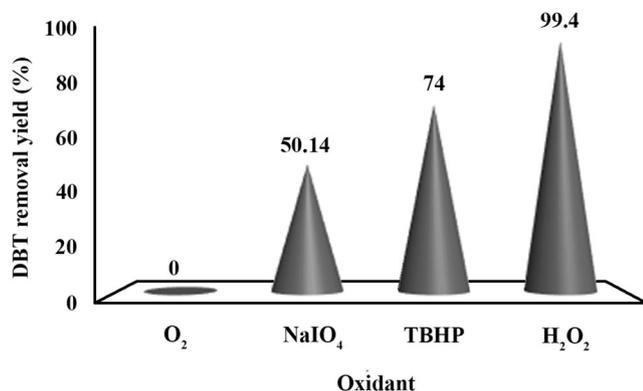


Fig. 7 Effect of different oxidants (O/S = 10) on the DBT oxidative removal (initial sulfur content = 500 ppm) at 25 °C and dosage catalyst = 0.03 g

Nilchi et al., 2011). The presence of these peaks in the FT-IR spectra of this compound confirms the formation of TiO₂-SiO₂ nanohybrids.

Though determination of the specific surface area (BET) of the synthesized hybrid nanoparticles with various TiO₂/SiO₂ molar ratios and selecting the best sample with the best crystallite and a proper specific surface area, the best molar ratio of TiO₂/SiO₂ was selected to improve its application in the process of removing sulfur compounds. To determine the structural properties of TiO₂ and TiO₂/SiO₂ nanoparticles, nitrogen adsorption/desorption isotherms were measured and analyzed at a temperature of 77 K. The structural characteristics of TiO₂ and TiO₂/SiO₂ nanohybrids with various molar ratios, including BET surface area, total pore volume, and average pore diameter, are shown in Table 2.

Figure 4 presents nitrogen adsorption/desorption isotherm curves of TiO₂ and TiO₂/SiO₂ samples with different SiO₂ contents. According to the IUPAC classification, all curves exhibited a type IV isotherm with a vertical hysteresis loop, and the adsorption/desorption branches are parallel to each other. Therefore, the pores in the samples are tubular and open at both ends. Hysteresis loop in the isotherm confirmed the existence of mesopores (Do Duong, 1998), indicating that all

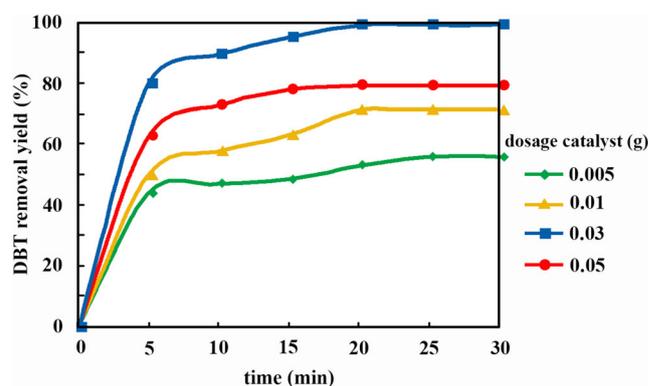


Fig. 8 Effect of catalyst dosage on the removal of DBT. Reaction condition: T = 25 °C, O/S = 10, initial sulfur content = 500 ppm

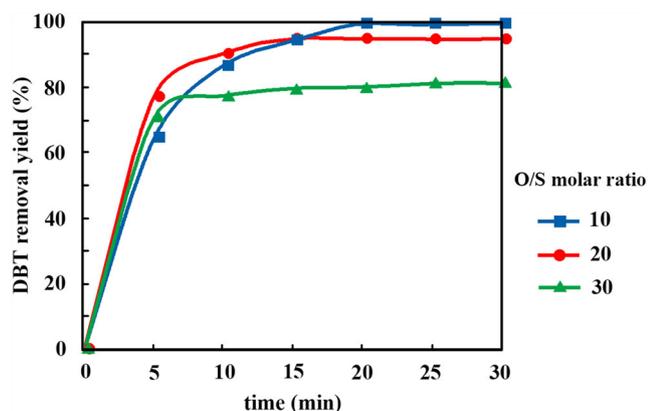


Fig. 9 Effect of O/S molar ratio on the removal of DBT. Reaction conditions: T = 25 °C, catalyst dosage = 0.03 g, t = 30 min, initial sulfur content = 500 ppm

samples are mesoporous materials. It was revealed that increasing the amount of SiO₂ in the nanohybrids structure leads to an increase in the specific surface area, which is the desired target. Accordingly, the TS-4 sample with the highest amount of silica was chosen for TEM and SEM analysis.

The TEM and SEM images of TS-4 nanohybrids are shown in Fig. 5. The SEM images (Fig. 5b) revealed that TS-4 nanohybrids are slightly agglomerated with a diameter range of 15–28 nm. The TEM image of nanohybrids demonstrated hexagonal and spherical morphology with minimum coagulation and sizes ranging between 3–9 nm (Fig. 5a).

Evaluation of catalytic activity

To evaluate the catalytic performance of TiO₂/SiO₂ nanohybrids with different molar ratios in the desulfurization process, several tests were carried out in the presence of H₂O₂ as a green oxidant. Desulfurization of the model fuel containing a solution of 500 ppm DBT in octane was performed at 25 °C with O/S molar ratio (nH₂O₂/nDBT) of 10 using 0.03-g catalyst within 20 min. From the results listed in Table 3, the catalytic activity of nanohybrids was poor (less than 5.0%) in

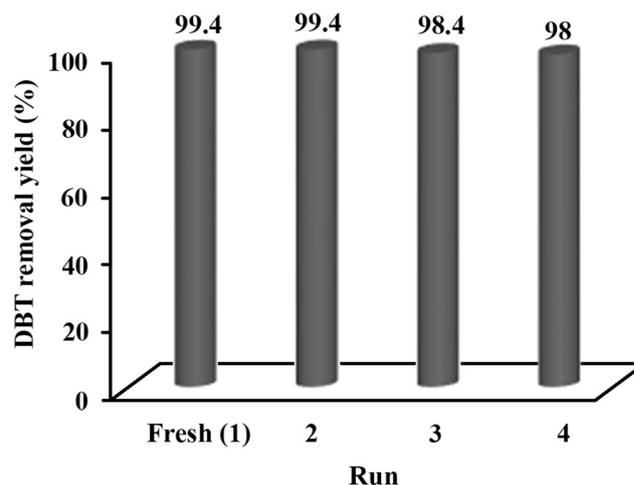


Fig. 10 Reusability of the catalyst. Reaction condition: T = 25 °C, O/S = 10, catalyst dosage = 0.03 g, t = 20 min, and initial sulfur content = 500 ppm

the absence of acetonitrile due to inadequate catalyst dispersion in the reaction medium and no favorable interaction between catalyst, the oxidizing agent (H₂O₂), and DBT molecules (Mojaverian Kermani et al., 2018). To investigate the effect of SiO₂ in the nanohybrid structure, the catalytic performance of pure TiO₂ was compared to TiO₂/SiO₂ nanohybrids with different molar ratios. According to the results listed in Table 3, desulfurization efficiency was significantly increased in the presence of TS-4 nanohybrids, which have the highest specific surface area. In other words, the increment in the catalyst specific surface area leads to the strong interaction between DBT and active sites of the catalyst. Therefore, the proper specific surface areas of the nanohybrids result in further removal of DBT. To obtain optimal conditions in the oxidation removal of DBT, the effects of various factors, including temperature, catalyst dosage, O/S molar ratio, and oxidizing agents, were investigated. Figure 6 shows the effect of temperature on DBT removal. The results indicate that 99.4% removal can be achieved at a temperature of 25 °C under the same reaction condition. By increasing the

Table 4 Comparison of catalytic performance of different catalysts in ODS reported in the literature

Catalyst	Cat. dosage (g)	t (min)	T (°C)	O/S molar ratio	S content (ppm)	Model fuel	Extractant	S removal (%)	Ref.
Cu/TS	0.4	240	70	19.9	-	iso-octane + thiophene	-	93	48
HPW-CeO ₂	0.02	30	30	6	500	n-octane + DBT	[C ₈ mim]BF ₄	99.4	13
HPW/mpg-C ₃ N ₄	0.12	150	60	8	100	n-octane + DBT	Methanol	100	31
HPW/SiO ₂	0.3	180	50	12	500	petroleum ether + DBT	Acetonitrile	100	49
HMT-PTA	0.033	180	60	20.7	910	hexane + DBT	Acetonitrile	99.9	50
Anatase TiO ₂	0.35	50s	70	10	100	n-octane + DBT	-	100	51
TiO ₂	0.1	2	70	50	300	n-octane + DBT	-	98	52
Co/Mn/Al ₂ O ₃	0.1	30	60	3	600	n-octane + DBT	-	98	53
TiO ₂ /SiO ₂ -40	0.03	20	25	10	500	n-octane + DBT	Acetonitrile	99.4	This work

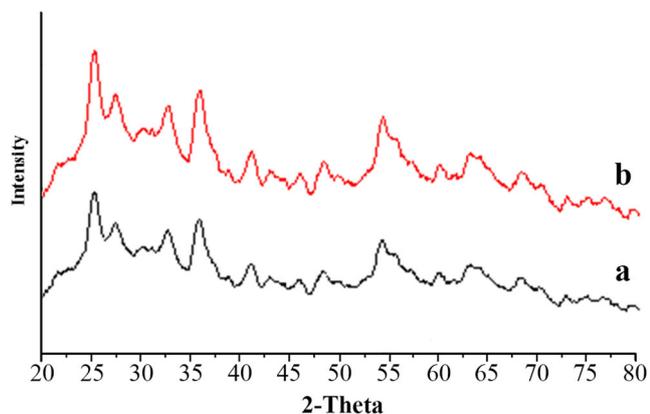


Fig. 11 XRD pattern of a fresh TS-4 catalyst (a) and after four times of reuse (b) in the DBT removal

temperature to 45 °C and 60 °C, almost complete removal was observed in 15 min. However, increase of temperature above 60 °C (up to 80 °C) has a reverse effect on the rate of removal due to the oxidant decomposition (Mojaverian Kermani et al., 2018). Regarding economic considerations and taking account of the time required for almost complete removal of DBT, the temperature of 25 °C was considered as optimal temperature. The effect of different oxidizing agents including TBHP, NaIO₄, O₂, and H₂O₂ in the presence of the TS-4 as the catalyst on DBT removal was also studied. From the results of Fig. 7, H₂O₂ is more effective than other oxidants.

The catalyst dosage in a reaction is a very important factor for the development of the process and economic estimation of the catalyst. To examine the effect of catalyst dosage in oxidative desulfurization, the process was carried out at different dosages of the TS-4 catalyst at 25 °C with an O/S molar ratio of 10. Figure 8 demonstrates that the oxidative removal of DBT becomes higher when the amount of the catalyst increases. This indicates that the availability of catalyst surface and active sites for proper interaction can play a crucial role in the reaction. With an increase of dosage from 0.03 g to 0.05 g, there is a gradual reduction in the DBT elimination, which is probably due to the accumulation and lack of active sites for

interactions. According to these results, the value of 0.03 g was considered for the continuation of the research.

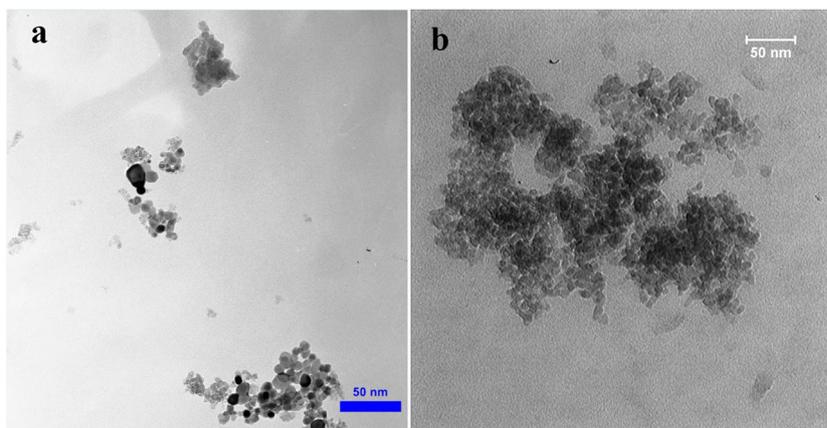
Furthermore, oxidation of DBT was investigated in the presence of the catalyst with different molar ratios of O/S [$n(\text{H}_2\text{O}_2)/n(\text{DBT})$] at 25 °C. Figure 9 indicates that DBT removal with O/S molar ratio of 10 has similar results as with O/S molar ratio of 20. It also shows that DBT removal decreased when the molar ratio was further increased. The reason is probably related to the spontaneous dissociation of hydrogen peroxide during the reaction. In general, in the presence of H₂O₂, two reactions are underway in this process: one is the oxidation reaction of DBT with H₂O₂ to the corresponding sulfone, and the other is spontaneous dissociation of H₂O₂. Accordingly, by increasing the molar ratio of O/S to more than 10, the amount of sulfur removal is reduced due to the production of water during the process (Mojaverian Kermani et al., 2018), which is an obstacle to the development of the reaction. Besides, the ratio of O/S = 10 was considered as the optimum ratio in this research.

In Table 4, the activity and catalytic performance of TS-4 were compared with other catalysts in the ODS process reported in the literature. It should be noted that the catalyst in this study was synthesized without any surface modification and it is successful in oxidative removal of DBT without using UV irradiation. According to Table 4, TS-4 is generally a proper catalyst in the oxidation desulfurization process.

Recovery of catalyst

To analyze the catalyst reusability, the catalyst was recovered and reused in the ODS process. In this regard, at the end of the reaction with fresh TS-4, the separation of the catalyst was done using centrifuge and decantation (3×5-mL ethanol). Afterward, it was dried under reduced pressure to be reused in the next run. The catalytic activity was gradually reduced as the number of catalyst reuse increased. However; the recycled catalyst demonstrated the catalytic activity with just a slight

Fig. 12 TEM of a fresh TS-4 catalyst (a) and after four times of reuse (b) in the DBT removal



drop in its performance (after four times) in the ODS process than the fresh catalyst (Fig. 10).

According to XRD and TEM images (Fig. 11 and 12), almost no change in morphology, structure, and particle size of used TS-4 catalyst was observed after four times recycling.

Mechanism of DBT oxidation

Our suggested mechanism in this paper is in agreement with previous reports for the oxidation of peroxides (Fig. S1) (Mokhtar et al., 2015). The first step is involved with the nucleophilic attack of H_2O_2 on the surface of TiO_2/SiO_2 , which results in the formation of complexes between these active species regarded as metal-peroxide intermediate (I). In the following, the nucleophilic attack of the sulfur atom in the dibenzothiophene compound (II) as a rich electron density moiety to complexes leads to the formation of dibenzothiophene sulfoxide (III) and water as a by-product. In the subsequent step, further oxidation of dibenzothiophene sulfoxide (III) by complexes gives rise to dibenzothiophene sulfone (V). As shown in Fig. S2, after the oxidation process, the extracted solvent phase demonstrates the peaks related to DBT sulfone, which proves the presence of sulfone during the oxidation reaction.

Conclusions

In this study, a novel, simple, and green procedure is introduced for the synthesis of TiO_2/SiO_2 nanohybrids. The desirable catalytic activity of TiO_2/SiO_2 nanohybrids was demonstrated via its efficiency in DBT removal, which enables sulfur elimination up to 99.4% without UV irradiation. The process was performed at 25 °C with O/S molar ratio of 10 and a catalyst amount of 0.03 g. Besides, the TS-4 catalyst in the presence of hydrogen peroxide exhibited higher catalytic oxidation capacity compared to the pure TiO_2 , TS-1, and TS-2. Moreover, the reusability evaluation of catalyst revealed no significant change in its performance after four times of recycling. It was found that sulfone moiety is produced as the only product of DBT catalytic oxidation. In summary, the TiO_2/SiO_2 nanohybrids provide a potent catalyst, which is promising in the refinement of fossil fuels via removal of resistant sulfur in compounds such as DBT in an oxidative desulfurization process.

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