

Porous SiO₂@ SiC Core-Shell nanospheres Functionalized with an Amino Hybrid of WO₃ as an Oxidative Desulfurization Catalyst --Manuscript Draft--

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Porous SiO₂@ SiC Core-Shell nanospheres Functionalized with an Amino Hybrid of WO₃ as an Oxidative Desulfurization Catalyst

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Abstract

A novel N-doped SiO₂@SiC core shell nanostructure has been synthesized using gelatin as a natural nitrogen-containing carbon source. It was then functionalized with amino groups for immobilization of active metal centers. Amino hybrid of tungsten oxide was supported on the surface of functionalized SiO₂@SiC core shell nanospheres by immobilization of oxodiperoxo complex of tungsten and by coordination of ethylenediamine to tungsten centers. The prepared hybrid has been characterized by FT-IR, XRD, TGA/DTA, SEM/EDS, and BET/BJH methods and its catalytic activity was investigated in oxidative desulfurization of model fuels. To evaluate the role of silicon carbide support, silica nanospheres alone were functionalized with the amino hybrid of tungsten oxide and its catalytic performance was compared. The results indicate that the SiC catalyst shows higher catalytic activity (99.9%, 160 min) compared to the SiO₂ analogue (61%, 160 min). Furthermore, the SiC catalyst shows higher stability and recyclability and exhibits no remarkable decrease in activity of catalyst after 5 runs.

Keywords: Silicon Carbide; Core shell; Tungsten Oxide; Hybrid; Oxidative Desulfurization.

1. Introduction

Use of sulfur-containing fuels causes many environmental problems and has major health impact. Hence, many efforts have been made to reduce the level of sulfur in fuels [1–4]. In recent years, several methods have been developed for the removal of sulfur compounds and reducing the sulfur levels in oil derivatives. Among different desulfurization methods, hydrodesulfurization as a conventional method has a high performance, but due to its difficult operating conditions such as high temperature and pressure and the use of hydrogen gas, many efforts have been made to find an alternative method to produce ultra-low sulfur fuels at mild conditions [5-8].

Nowadays, oxidative desulfurization (ODS) is attracting significant research interest due to its mild operating conditions, easy lower-cost procedures, and conventional equipment. Another advantage of ODS is its higher efficiency for removing the aromatic sulfur compounds such as thiophene and its derivatives [8,9]. In this process, the sulfur species in the fuel are converted to the corresponding sulfones by appropriate oxidant and then they are separated by extraction or adsorption. In this respect, the catalyst is the most important parameter in the ODS process. Various transition metals oxides such as W, Mo, V, Ti, Co, and Fe have been used as efficient catalysts in ODS process [10–14].

The surface area and the number of active sites are important factors in the effectiveness of catalysts. Immobilization of metal oxide catalysts on the surface of porous supports is an effective way to increase the accessible surface area, to obtain homogenous distribution of metal oxide, and increase the number of active sites. Silica, alumina, carbon, and silicon carbide nanostructures have been used as the catalyst supports to design heterogeneous ODS catalysts with optimized properties [15–21].

Among these materials, silicon carbide, due to its unique properties such as high surface area, high chemical, mechanical and thermal stability, is an appropriate candidate for various catalytic process [19-26]. In the present work, a new catalyst based on an amino-functionalized SiO₂@SiC core-shell nanospheres has been synthesized and immobilized with amino hybrid of tungsten oxide and the role of the silicon carbide support and tungsten hybrid was investigated in ODS reaction.

2. Experimental

2.1 Materials and Methods

All chemicals were of analytical grade and were used without further purification. Tungstic acid and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich and gelatin, ethylenediamine, tetraethylorthosilicate (TEOS), (3-aminopropyl)triethoxysilane, Mg powder (0.06-0.3 μ m), and hydrochloric acid (37%) were obtained from Merck and used for synthesis of the hybrid. Thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT), n-octane, n-dodecane, acetonitrile, and hydrogen peroxide (30%) were obtained from Merck and used for catalytic study.

FT-IR spectra were recorded in the range of 400-4000 cm⁻¹ by a Bruker, Vector spectrometer. Crystallographic data of samples were investigated by powder X-ray diffraction (XRD), were obtained by a Bruker, Axs using CuK α radiation with λ = 1.54060Å in the range 2 θ = 10–80°. The morphologies of nanostructures were characterized by a scanning electron microscope (TESCAN, VEGA3) equipped with a X-ray energy dispersive spectroscopy (EDX). Measurement of porosity and specific surface areas of samples were taken with a Belsorp mini

instrument. A Netzsch, TGA 209 F1 instrument was used for thermal gravimetric analysis. Products of ODS were determined by gas chromatography (GC), Faraz Gostar, TG 2552, using (Flame ionization) FID detector.

2.2 Synthesis of SiO₂@SiC core-shell nanospheres

Silica nanospheres were synthesized via stober method according to previous literature [27]. Ethanol, water, and ammonia were mixed with a volume ratio of 20:2:1 and stirred for 15 min and then 1 ml of TEOS was added dropwise to the 23 ml of above solution to prepare the silica nanospheres.

A 12 ml of an aqueous solution of gelatin (12 ml) containing 1 M CTAB was prepared and mixed with the same volume of above silica nanospheres solution, then the mixture was transferred into a 60 ml Teflon lined autoclave and heated at 170 °C for 3 h. The yellow-white precipitate was filtered and dried at 70 °C for 24 h. Then the sample was mixed with Mg powder (Si: Mg molar ratio 1: 2) and heated at 800 °C under N₂ atmosphere by a heating rate of 5 °C/min. Finally, the obtained SiO₂@SiC core-shell was immersed in 2 M HCl solution for 48 h to eliminate the produced MgO.

2.3 Amino Functionalization of SiO₂@SiC core-shell (NH₂-SiO₂@SiC)

1.5 g of SiO₂@SiC powders were mixed with 40 ml toluene and 2 mL of 3-aminopropyltriethoxysilane was added to this solution. Then, the prepared solution was refluxed at 100 °C for 24 h. Finally, the brown precipitate was filtered and dried at 80 °C for 24 h. This compound is named NH₂-SiO₂@SiC.

2.4 Immobilization of tungsten oxide ($\text{WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$)

To immobilize the tungsten oxide on the surface of functionalized $\text{SiO}_2\text{@SiC}$, 2.5 g of tungstic acid was dissolved in 60 mL of H_2O_2 at 40 °C to obtain oxodiperoxo tungsten solution ($\text{WO}(\text{O}_2)_2$). Then, 1 g of synthesized $\text{NH}_2\text{-SiO}_2\text{@SiC}$ was added to this solution and stirred for 24 h at room temperature. The obtained product was filtered and dried at 60 °C, and named $\text{WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$.

2.5 Coordination of ethylenediamine ($\text{N-WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$)

In this step, 1 g of synthesized $\text{WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$ was dispersed in 50 mL of ethanol. Then, 2 mL of ethylenediamine was added dropwise to the above solution and refluxed at 90 °C for 24 h. Finally, the product was centrifuged, washed two times with ethanol, and dried at 70 °C for 24 h. This compound was named $\text{N-WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$.

The above synthesis procedures are schematically summarized in Fig. 1.

2.6 Synthesis of corresponding silica hybrid ($\text{N-WO}_3\text{-NH}_2\text{-SiO}_2$)

In order to investigate the effect of silicon carbide support on the removal of sulfur compounds, the corresponding silica hybrid was synthesized as well. For this purpose, silica nanospheres synthesized again via the stober method were functionalized with amine, tungsten oxide, and ethylenediamine in the same way as $\text{SiO}_2\text{@SiC}$ hybrid. The synthesized sample was named $\text{N-WO}_3\text{-NH}_2\text{-SiO}_2$.

2.7 Catalytic Studies

In a typical run, various model fuels such as DBT, BT, and TH with different sulfur concentration (100, 300, 500, 700, and 1000 ppm) were prepared by dissolving them in n-octane. The ODS reaction was done in a 25 ml flask equipped with a magnetic stirrer and a water bath at

various temperature (25, 40, 50, and 65 °C). First, a certain amount of catalyst (10-30 mg), 2 ml of model fuel, 1 ml of acetonitrile as an extractive solvent, and n-dodecane as an internal standard were mixed together by stirring in a given temperature. Then 0.02- 1 ml of H₂O₂ as an oxidant was added to system. Every 20 min, a small amount of the sample was collected and injected into the GC to investigate the conversion percent of sulfur compounds.

3. Results and Discussion

3.1 Characterization

The chemical grafting of various functional groups was verified by FT-IR analysis. Fig. 2a-d shows FT-IR spectra of SiO₂@SiC and its functionalized hybrids. The peak at about 825 cm⁻¹ shows the formation of a Si-C bond in the SiO₂@SiC structure (Fig. 2a). This bond is shifted to a lower frequency (820 cm⁻¹) during the functionalization of SiC with APTES (Fig. 2b). Immobilization of tungsten oxide has also shifted Si-C bond to 818 cm⁻¹ in WO₃-NH₂-SiO₂@SiC and N-WO₃-NH₂-SiO₂@SiC hybrids (Fig. 2c,d). The peaks at about 460 and 1075 cm⁻¹ are assigned to the Si-O-Si bond which is related to SiO₂ core. In Fig. 2b the appeared bonds at about 2840-2930 cm⁻¹ and 1480-1547 cm⁻¹ correspond to the propyl group and N-H bond, respectively which indicates the existence of 3-aminopropyltriethoxysilane. The new peaks at 607 and 845 cm⁻¹ in Fig. 2c and the peaks at 585 and 865 cm⁻¹ in Fig. 2d correspond to W=O and W(O-O) and confirm the immobilization of oxoperoxo tungsten complex (WO(O₂)₂) onto the NH₂-SiO₂@SiC support [11]. After coordination of ethylenediamine, the C-H and N-H bonds were intensified (Fig. 2d). For comparison, FT-IR spectra of silica alone and its functionalized hybrids are displayed in Fig. S1.

XRD patterns of SiO₂@SiC and its functionalized hybrids with amino silan, tungsten oxide, and ethylenediamine are shown in Fig. 3. Diffraction pattern of bare SiO₂@SiC indicate weak diffraction peaks at $2\theta = 35.75, 60.40,$ and 69.23 are assigned to (102), (110), and (202) planes of hexagonal structure of 6H-SiC (JCPDS 29-1128) (Fig. 3a). The low intensity of SiC peaks can be attributed to the amorphous nature of SiC structure that grows on the SiO₂ core. Also, the three peaks at about $28.42, 47.25,$ and 56.17° can be attributed to (111), (220), and (311) planes of cubic phase of silicon (JCPJDS 27-1402) (Fig. 3a). After amino-functionalization of SiO₂@SiC sphere, the same pattern with a slight shift to a higher degree was observed (Fig. 3b). The XRD pattern of WO₃-NH₂-SiO₂@SiC shows the appearance of diffraction peaks at $2\theta=16.12, 19.79, 23.86,$ and 29.56° which are assigned to (020), (011), (120), and (031) planes of orthorhombic tungsten oxide (JCPDS 43-0679) and existence of peaks at $2\theta=11.88, 24.58,$ and 27.40 are related to (010), (001), and (011) planes of monoclinic tungstic acid (JCPDS 18-1420). This result obviously confirms successful chemical grafting of WO₃ on the surface of SiO₂@SiC core-shell (Fig. 3c). N-WO₃-NH₂-SiO₂@SiC hybrid shows only a slight shift to the higher degree (Fig. 3d).

Thermogravimetric analysis (TGA/DTA) of N-WO₃-NH₂-SiO₂@SiC are shown if Fig. 4. The TGA curve shows three weight losses at $25-100^\circ\text{C}$ (1.14 %), $120-320^\circ\text{C}$ (2.40 %), and $340-540^\circ\text{C}$ (6.49 %). The negligible weight loss in the first step is attributed to evaporation of traces of water on the surface of the catalyst. The weight loss about 2.4 % in the second step is related to the loss of peroxo groups of tungsten complex (W(O)(O₂)₂) and their transformation into the oxo form (WO₃). Moreover, the weight loss about 6.49 % in the third step is attributed to the degradation of amine groups in the inorganic-organic hybrid on the SiO₂@SiC core-shell. The

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4 result of TGA/DTA analysis indicates the successful modification of $\text{SiO}_2@\text{SiC}$ with amino
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6 silane, tungsten oxide, and ethylenediamine.
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10 As mentioned, $\text{SiO}_2@\text{SiC}$ core-shell was synthesized from silica nanospheres. The
11 morphology of silica nanospheres alone and its modified inorganic-organic hybrid of WO_3 are
12 shown in Fig. 5. The synthesized silica nanospheres show a diameter of 380-550 nm (Fig. 5a).
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14 Fig. 5b shows that the amino-functionalization of silica nanosphere did not change the
15 morphology of silica. After immobilization of tungsten oxide, the rod-like morphology of WO_3
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17 is observed on the surface of the silica sphere (Fig. 5c,d).
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25 The morphology of synthesized $\text{SiO}_2@\text{SiC}$ core-shell and its modified structures are
26 presented in Fig. 6. Fig. 6a shows the SEM image of $\text{SiO}_2@\text{SiC}$ core-shell which shows a larger
27 diameter than the SiO_2 sphere ranging within 430-630 nm. It confirms the formation of SiC shell
28 on the surface of the silica sphere. Fig. 6b displays the SEM image of amino-functionalized
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30 $\text{SiO}_2@\text{SiC}$ which shows the same morphology as $\text{SiO}_2@\text{SiC}$ core-shell. SEM images of
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32 immobilized $\text{SiO}_2@\text{SiC}$ with tungstic oxide also show the remarkable needle-like structure of
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34 tungsten oxide which is distributed on the surface of $\text{SiO}_2@\text{SiC}$ nanospheres (Fig. 6c,d).
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43 Elemental analysis is reported in Table 1. The results show 4.6 % of N in the $\text{SiO}_2@\text{SiC}$ core-
44 shell which is related to the doping of nitrogen due to the use of gelatin as a C source [19]. After
45 amino-functionalization of $\text{SiO}_2@\text{SiC}$, the amount of N increases to 7.7 % which confirm the
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47 successful functionalization of SiC surface with amino groups. In the $\text{WO}_3\text{-NH}_2\text{-SiO}_2@\text{SiC}$
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49 sample, 8.8% tungsten was observed which shows the immobilization of WO_3 on the surface of
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51 functionalized SiC. The final modification with ethylenediamine also shows the increase of
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53 nitrogen content from 7.4 % to 7.8 % which proves the formation of amino-hybrid of tungsten
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Fig. 7 characterizes the porosity of SiO₂@SiC core-shell and its modified N-WO₃-NH₂-SiO₂@SiC catalyst. After modification of SiO₂@SiC core-shell with amine and tungsten oxide, the specific surface area increased from 31 m²/g in SiO₂@SiC to 94 m²/g in N-WO₃-NH₂-SiO₂@SiC catalyst (Table 2). The results clearly indicate that the surface area increased after surface modification. Also, the result shows the decrease of pore diameter after modification of surface from 30.8 nm in SiO₂@SiC to 21.6 nm in N-WO₃-NH₂-SiO₂@SiC catalyst (Table 2). As shown in Table 2, after functionalization of SiO₂@SiC, a considerable decrease in the micropore content from 18.9 % in SiO₂@SiC to 7.7 % in N-WO₃-NH₂-SiO₂@SiC was observed. It can be justified by filling the smaller pores of SiO₂@SiC with the amino group and tungstic oxide nanoparticles.

3.2 Catalytic Studies

3.2.1 Effect of temperature

In the desulfurization system, the temperature is an important parameter. Fig. 8 exhibits the effect of different temperature (25, 40, 55, and 65 °C) on the oxidative desulfurization of model fuel (500 ppm(S) of DBT). The result indicates that by increasing of the temperature clearly enhances the catalytic activity of N-WO₃-NH₂-SiO₂@SiC. At 25 °C, the conversion observed was the lowest (34% after 160 min). The conversion increased to 68% at 40 °C and reached 100% at 55 °C. By increasing the temperature to 65 °C, the rate of reaction was increased and the conversion was assured to 100% in 120 min.

3.2.2 Effect of the catalyst amount

Fig. 9 shows the effect of catalyst amount on the oxidation of model fuel (500 ppm(S) of DBT). As the results show, by increasing the amount of catalyst (5 to 30 mg), the conversion of DBT increases. When 5 mg of catalyst was used, the 95.5 % sulfur removal was observed, while by increasing the amount of catalyst to 10 mg, 100 % sulfur removal was obtained after 160 min. Increase the amount of catalyst to 20 and 30 mg enhanced the rate of conversion and 100% conversion was assured after 140 and 120 min, respectively.

3.2.3 Effect of oxidant

The oxidant is another key parameter in oxidative desulfurization. Fig. 10. depicts the oxidation of DBT in the presence of various amounts of hydrogen peroxide (0.02 to 1.5 ml). By using 0.02 ml of H_2O_2 , only 81% sulfur removal was observed, while by increasing the amount of oxidant to 0.5 ml, complete sulfur removal was obtained. Also, results indicate that by increasing the amount of oxidant to 1.5 ml, the rate of the reaction increased.

3.2.4 Effect of model fuel (DBT) concentration

To assess the catalytic performance of $N-WO_3-NH_2-SiO_2@SiC$ catalyst, various concentrations of sulfur in a model fuel (DBT) (100, 300, 500, 700, and 1000 ppm) were tested. As can be seen in Fig. 11, by decreasing the concentration of sulfur from 1000 to 300 ppm, the conversion and also the rate of reaction increased from 86 to 100 %. But in the lowest concentration (100 ppm), the conversion decreased to 88 %. This can be explained by decreasing the amount of adsorbed sulfur compound on the surface of the catalyst in the dilute solution which can decrease the sulfur removal ability of the catalyst.

3.2.5 Effect of different sulfur compounds

Fig. 12 exhibits the effect of different sulfur compounds (500 ppm) on the performance of the catalyst in ODS reaction. Results show 99, 96, and 78 % sulfur removal for DBT, BT, and TH, respectively. These results can be explained by the electron density of sulfur atoms at these compounds. By increasing the electron density of the sulfur atom, the reactivity increases due to the increase of the orbital level [28]. The electron density of sulfur in DBT, BT, and TH compounds have been reported to be 5.76, 5.74, and 5.69, respectively [28]. So, the highest removal was observed in DBT which has higher electron density.

3.2.6 Recovery of the catalyst

To investigate of reusability of N-WO₃-NH₂-SiO₂@SiC catalyst, the catalyst was separated from system by centrifuging, dried at 80°C, and used in another ODS experiment without washing. The results show that the catalytic activity of N-WO₃-NH₂-SiO₂@SiC catalyst did not change until 3 runs, but a 10 % decrease on sulfur removal was observed after 5 runs (Fig. 13). This decrease in the catalytic activity of catalyst occurred due to the absorption of sulfone products on the surface of catalyst which can be easily removed by washing catalyst with acetonitrile [20]. The conversion of the washed catalyst remains 100% even after 5 runs.

Fig. 14 shows the FT-IR spectrum of fresh, used, and washed N-WO₃-NH₂-SiO₂@SiC catalyst. FT-IR spectra of used catalyst (after 5 runs) indicate some peaks assigned to adsorbed sulfone compounds on the surface of the used catalyst. While FT-IR spectra of washed catalyst is similar to the fresh catalyst and there are no peaks related to products on the surface of the catalyst.

To confirm the oxidative property of N-WO₃-NH₂-SiO₂@SiC nanostructure, the reaction was repeated without catalyst, without oxidant, and only by using SiO₂@SiC substrate. By using the oxidant, without the catalyst, only the 18% conversion observed. But, by using the catalyst, without oxidant, 41% conversion was observed which is related to the adsorption of DBT on the surface of the catalyst. Also, the catalytic property of SiO₂@SiC core-shell as the support of catalyst was investigated in the presence of oxidant. The result shows a 57% sulfur removal which confirms the catalytic property of SiC in the ODS reaction [19]. According to previous literature, SiC can adsorb oxidant via the positive charged Si atoms and produce radicals to oxidize the sulfur compounds [29].

To further highlight the catalytic properties of silicon carbide, N-WO₃-NH₂-SiO₂ was compared with corresponding SiC catalyst (N-WO₃-NH₂-SiO₂@SiC) under the same conditions. The same amount of active site (WO₃) was used for each catalyst according to the amount of tungsten (Table 1). The results indicate that silica catalyst only removes 61% sulfur after 160 min, while SiC catalyst reached 100% sulfur removal after 160 min. This result clearly exhibits the higher performance of SiC as catalyst support compared to SiO₂. The higher catalytic activity of SiC can be explained by the higher surface area of SiC catalyst and its property to possess a positive Si atom in the SiC structure, to adsorb oxidant, produce radicals and thus accelerate the reaction.

Conclusions

N-doped SiO₂@SiC core-shell nanospheres were synthesized through the reaction of silica nanospheres with gelatin as a carbon source to produce SiC on the surface of silica. The synthesized SiO₂@SiC core-shell nanoparticles were functionalized with amino groups and then stabilized with tungsten oxide. Finally, diethylenamine was used to produce the amino-hybrid of WO₃ on the surface of silicon carbide core-shell. To evaluate the catalytic activity of this synthesized hybrid, the removal of sulfur compounds were investigated by using N-WO₂-NH₂-SiO₂@SiC as the catalyst, acetonitrile as an extracting solvent, and hydrogen peroxide as an oxidant. This hybrid catalyst shows better catalytic activity compared to its corresponding silica catalyst.

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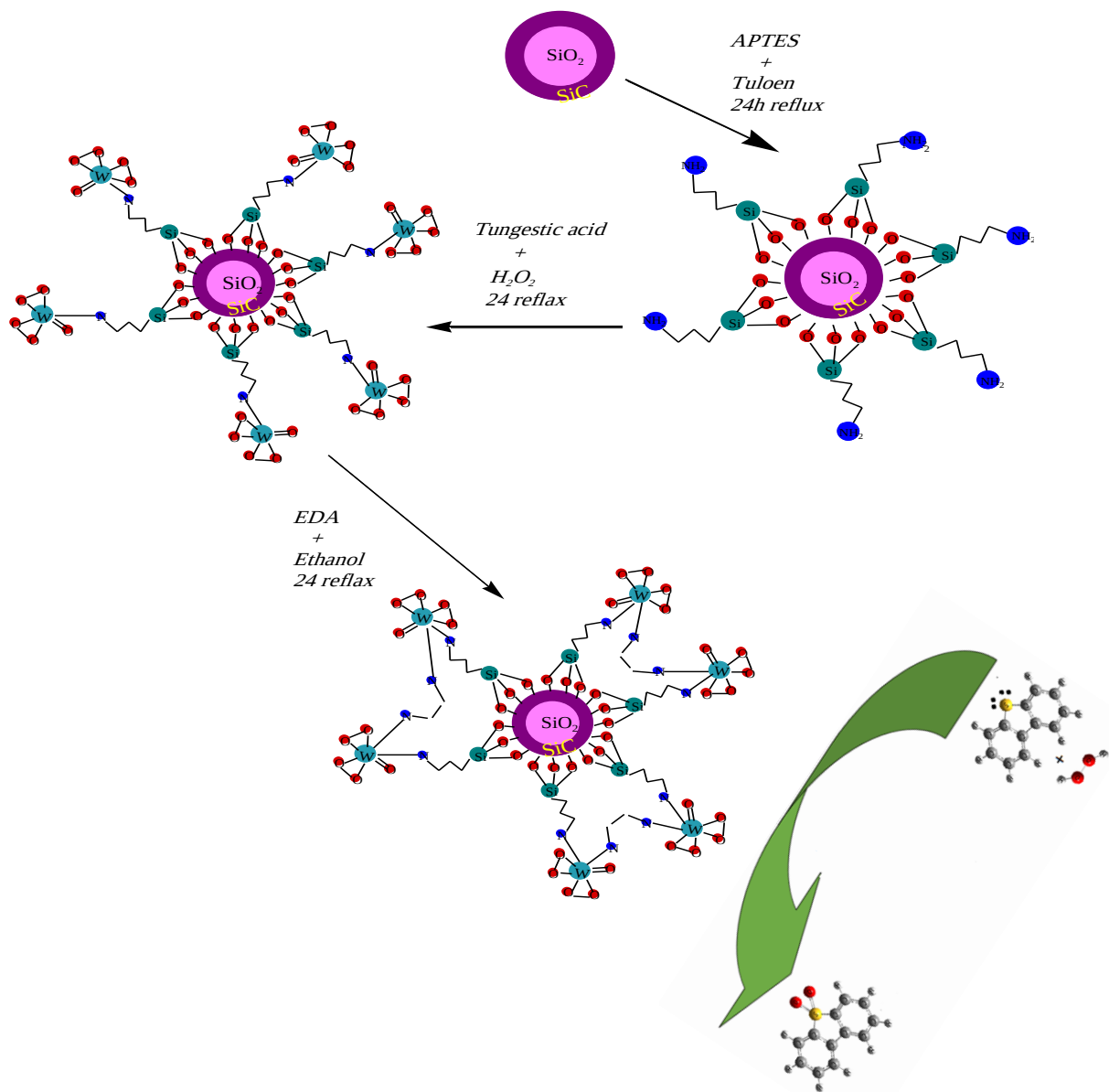


Figure 1 Scheme of procedures for synthesis of N-WO₃-NH₂-SiO₂@SiC catalyst and its catalytic reaction.

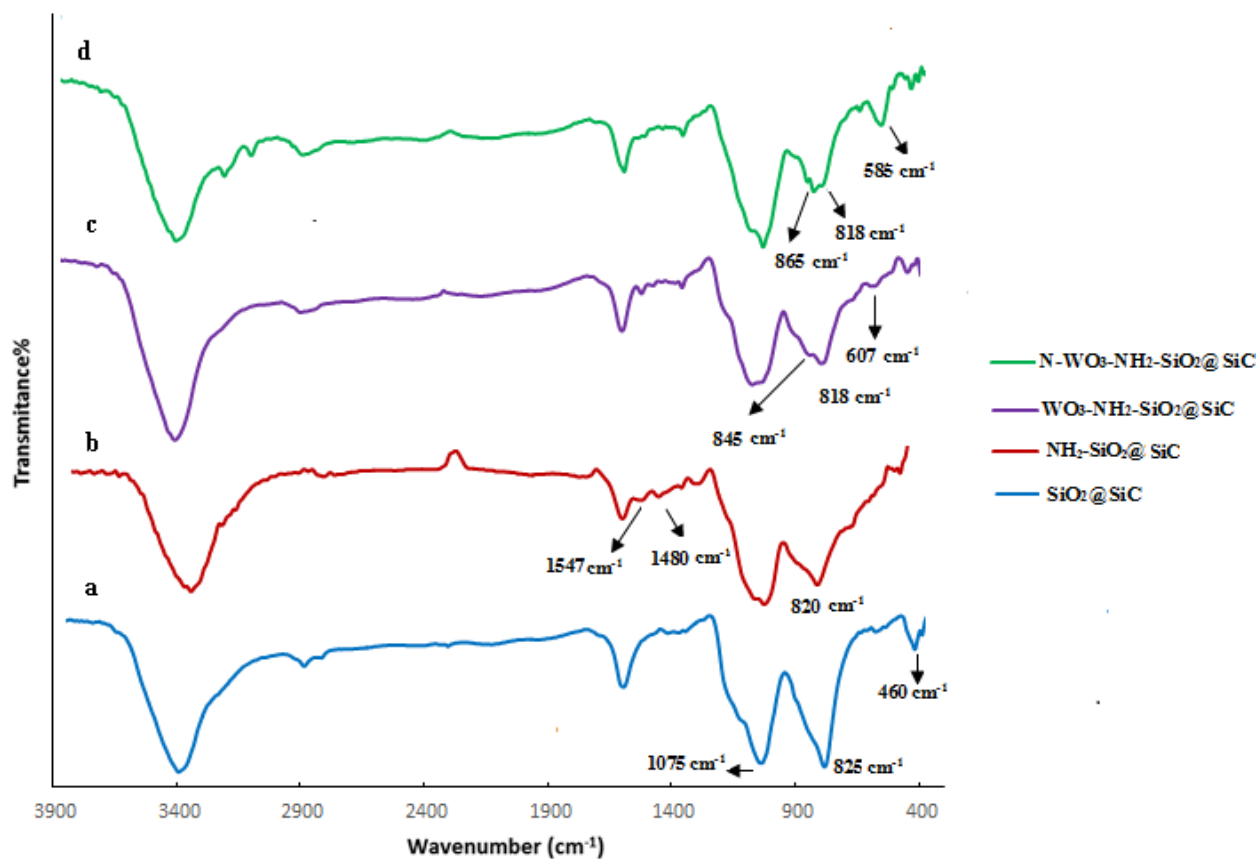


Figure 2 FT-IR spectra of $\text{SiO}_2@\text{SiC}$ and its functionalized hybrids.

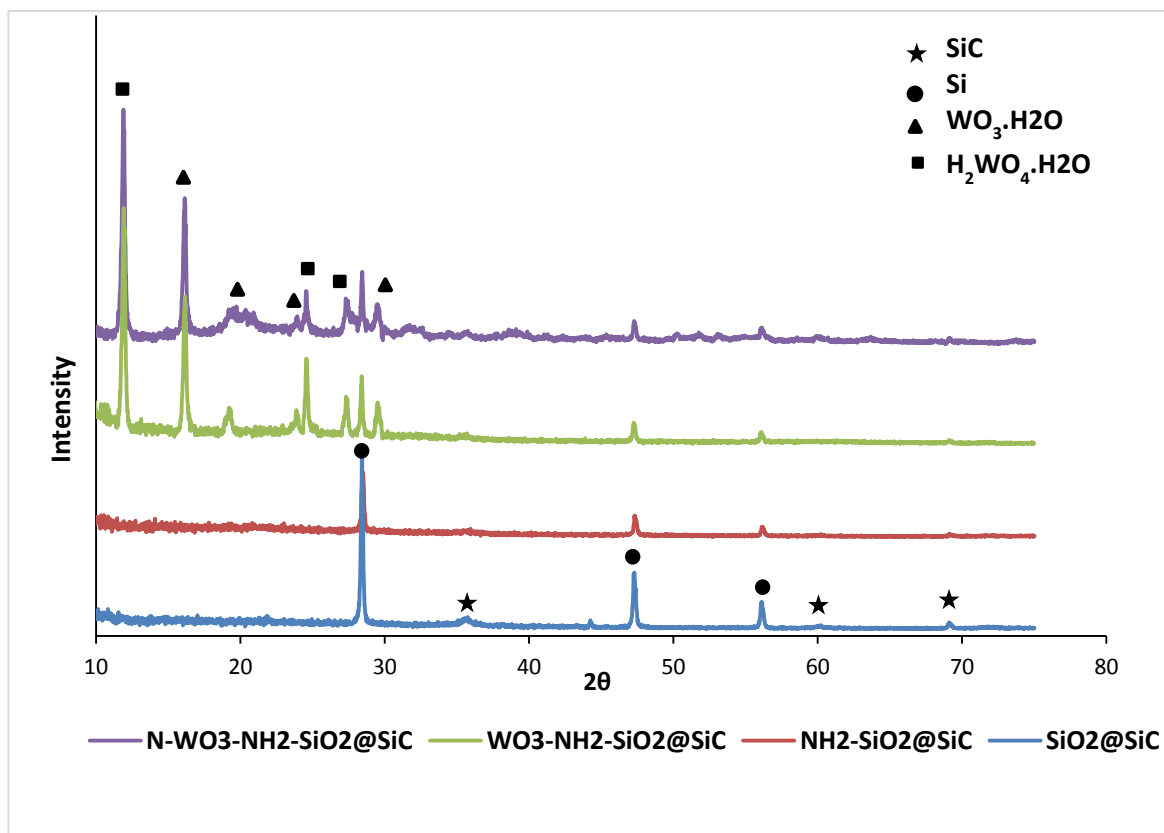


Figure 3 XRD patterns of $\text{SiO}_2@\text{SiC}$ and its functionalized hybrids.

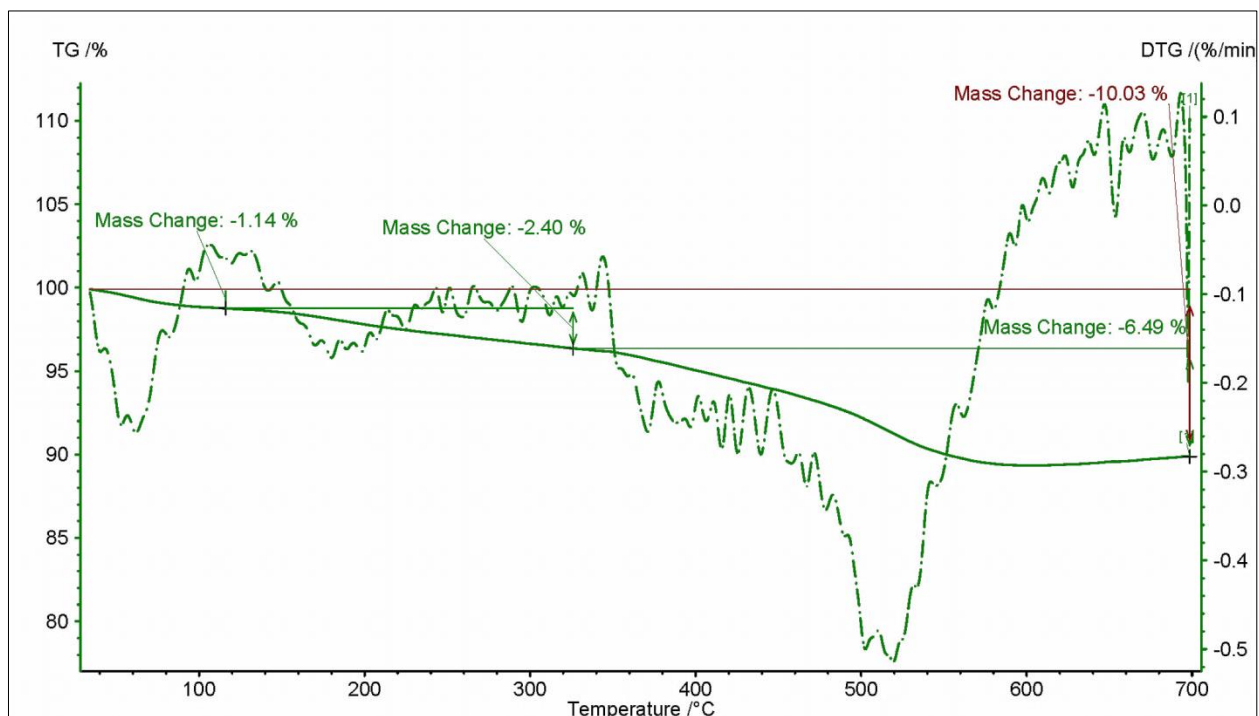


Figure 4 TGA/DTA curves of N-WO₃-NH₂-SiO₂@SiC catalyst.

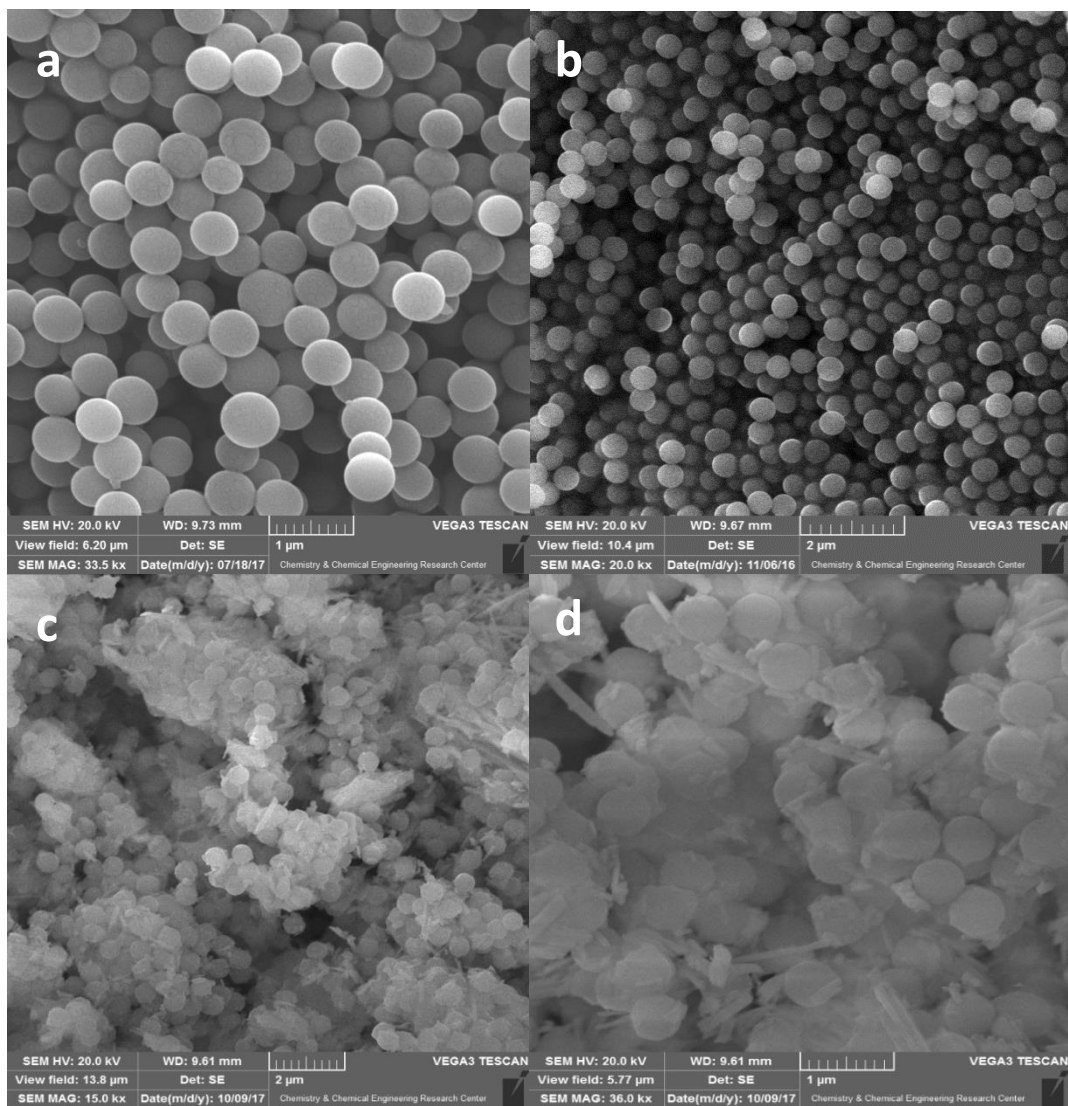


Figure 5 SEM of SiO_2 (a), $\text{NH}_2\text{-SiO}_2$ (b), $\text{WO}_3\text{-NH}_2\text{-SiO}_2$ (c), $\text{N-WO}_3\text{-NH}_2\text{-SiO}_2$ (d)

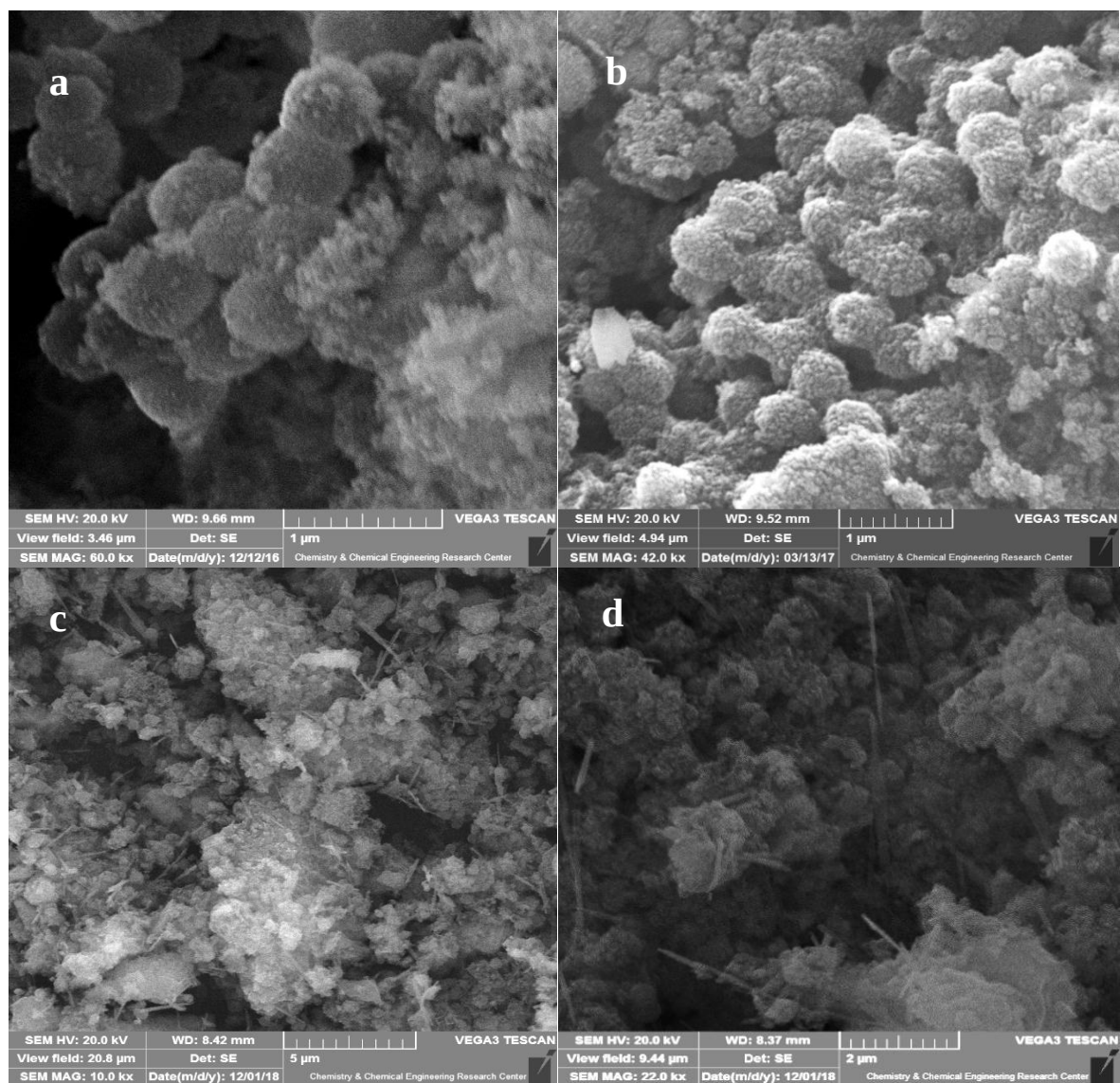


Figure 6 SEM images of $\text{SiO}_2@\text{SiC}$ (a), $\text{N-SiO}_2@\text{SiC}$ (b), $\text{WO}_3\text{-NH}_2\text{-SiO}_2@\text{SiC}$ (c), and $\text{N-WO}_3\text{-NH}_2\text{-SiO}_2@\text{SiC}$ (d).

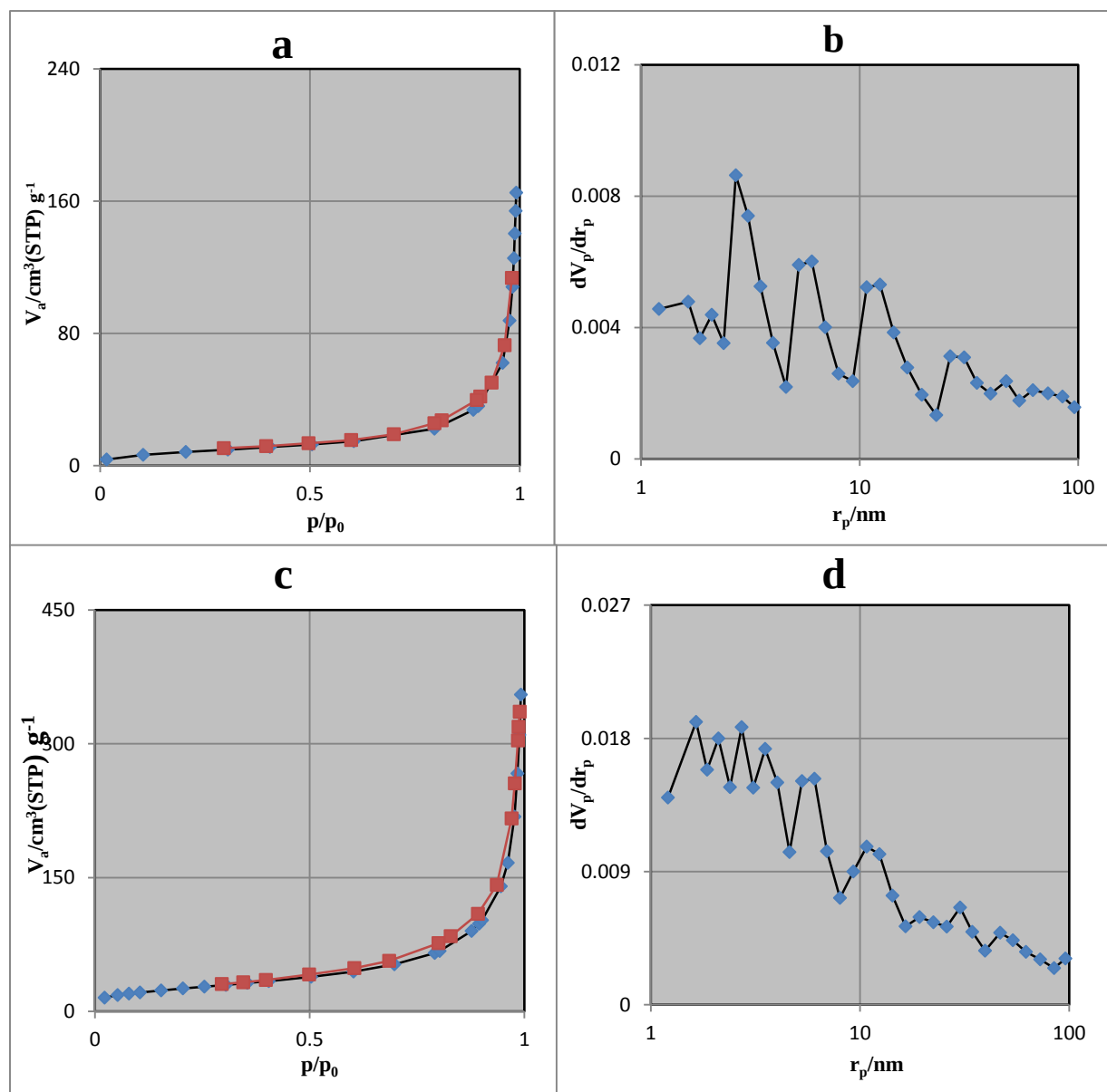


Figure 7 N₂ adsorption/desorption isotherms and pore size distributions of SiO₂@SiC core-shell (a,b) and N-WO₃-NH₂-SiO₂@SiC (c,d).

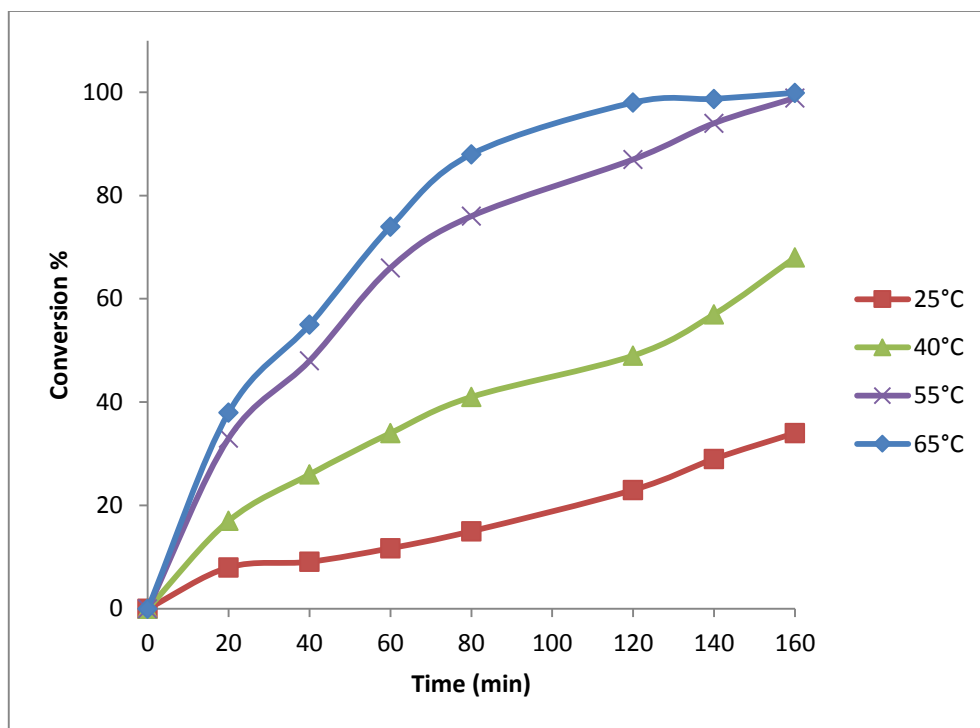


Figure 8 Effect of reaction temperature on oxidation of DBT at optimized condition: 10 mg N-WO₃-NH₂-SiO₂@SiC catalyst, 2 ml of model fuel 500 ppm (S), 0.5 ml hydrogen peroxide (30%), 1 ml acetonitrile.

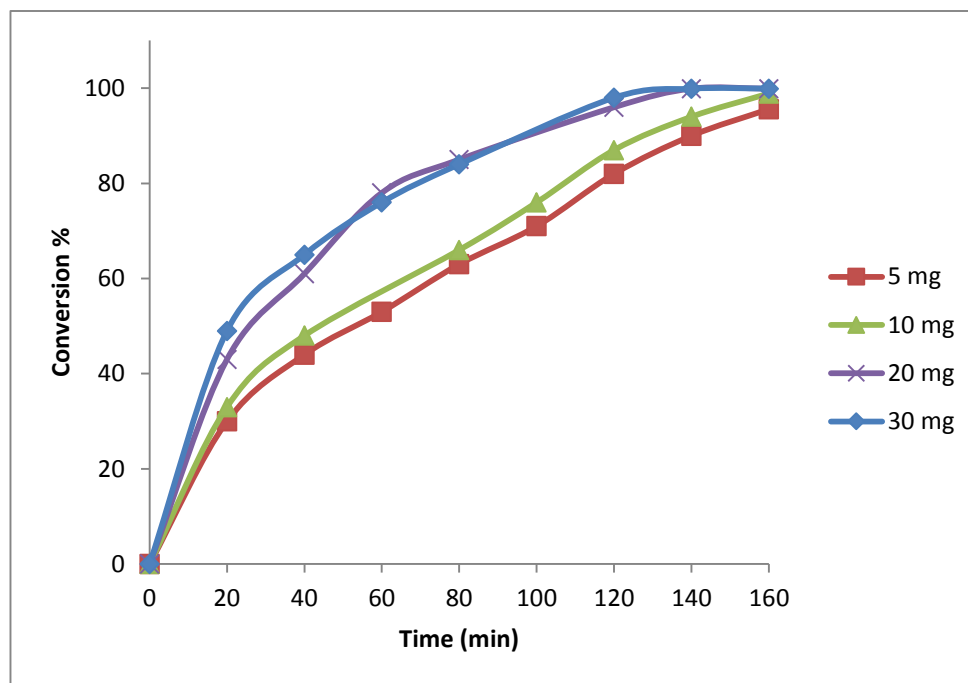


Figure 9 Effect of amount of catalyst (N-WO₃-NH₂-SiO₂@SiC) on oxidation of DBT at optimized condition: 2 ml of model fuel 500 ppm(S), 0.5 ml hydrogen peroxide (30%), 1 ml acetonitrile, 55 °C.

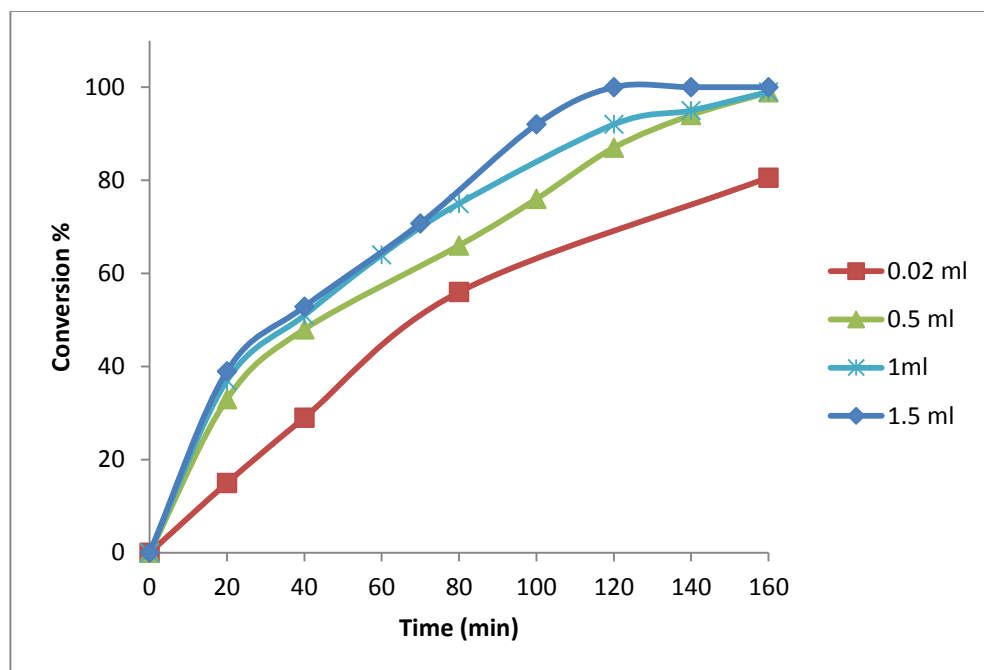


Figure 10 Effect of amount of oxidant on oxidation of DBT at optimized condition: 10 mg N-WO₃-NH₂-SiO₂@SiC catalyst, 2 ml of model fuel 500 ppm(S), 1 ml acetonitrile, 55 °C.

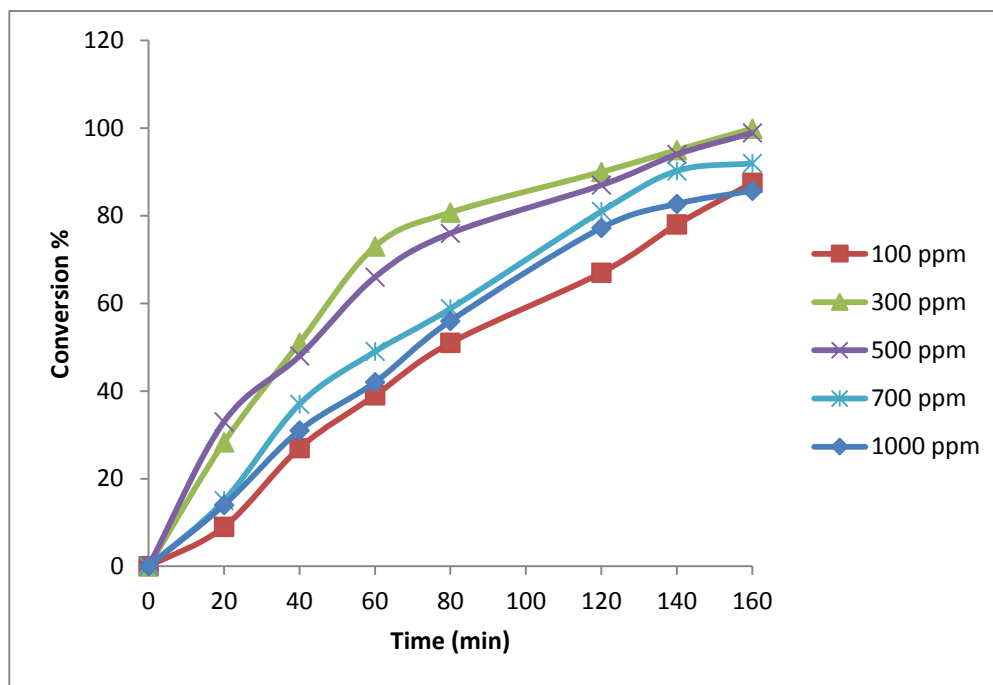


Figure 11 Effect of reagent concentration on oxidation of DBT at optimized condition: 10 mg N-WO₃-NH₂-SiO₂@SiC catalyst, 2 ml of model fuel, 0.5 ml hydrogen peroxide (30%), 1 ml acetonitrile, 55 °C.

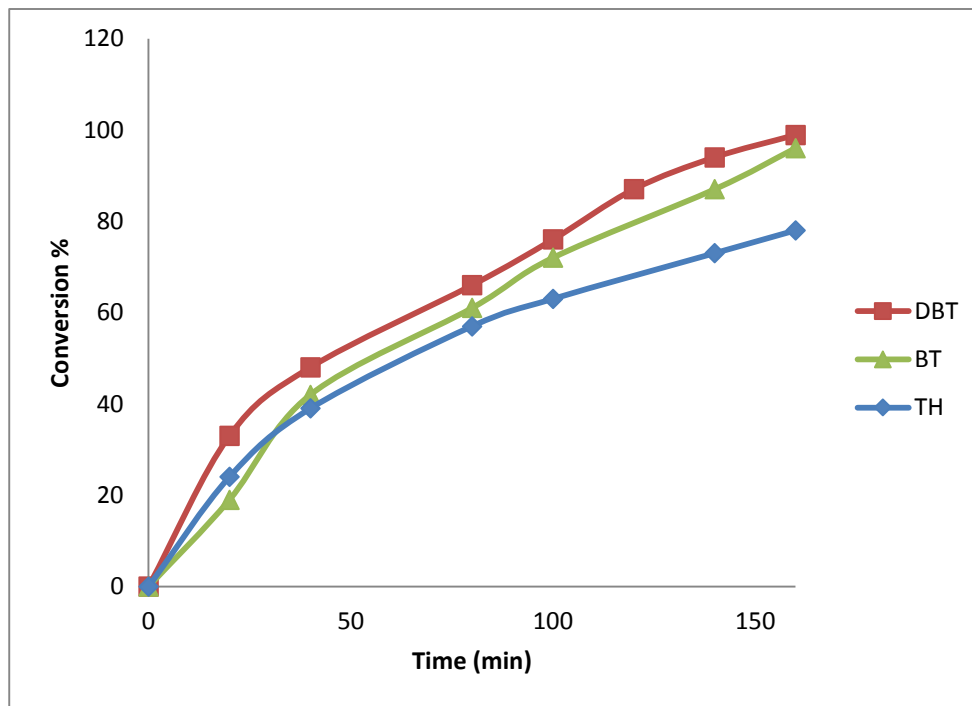


Figure 12 Effect of different kind of sulfur compound in ODS reaction at condition: 10 mg N- $\text{WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$ catalyst, 2 ml of model fuel (500 ppm), 0.5 ml hydrogen peroxide (30%), 1 ml acetonitrile, 55 °C.

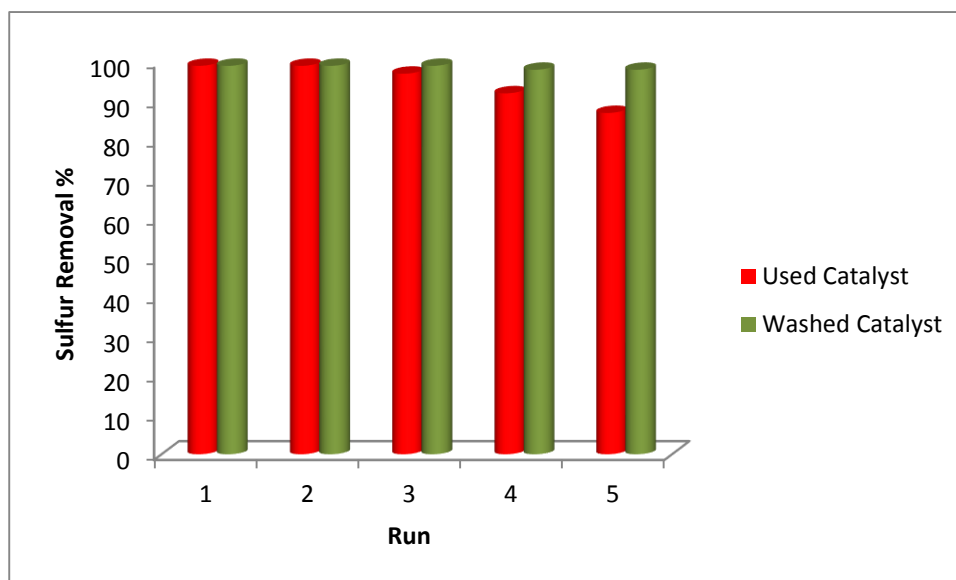


Figure 13 Recovery of $\text{N-WO}_3\text{-NH}_2\text{-SiO}_2\text{@SiC}$ catalyst without washing (used catalyst) and after washing (washed catalyst).

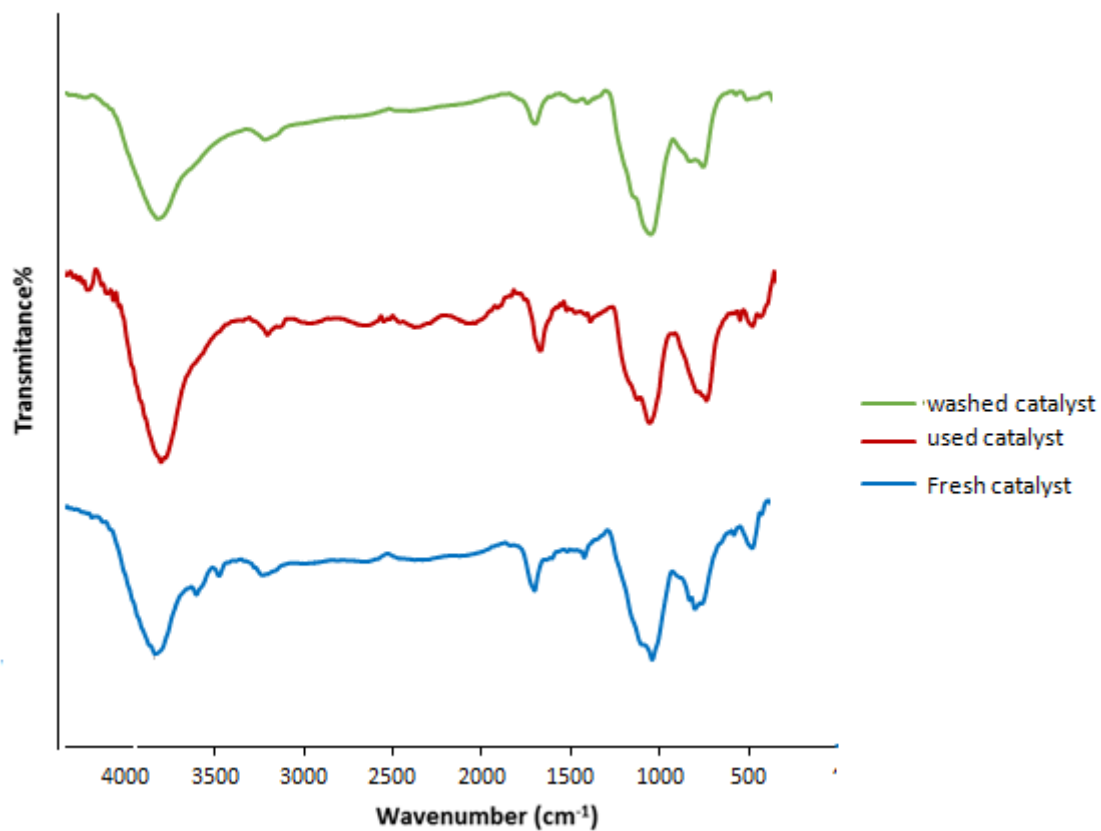


Figure 14 FT-IR characterization of fresh, used, and washed N-WO₃-NH₂-SiO₂@SiC catalyst.

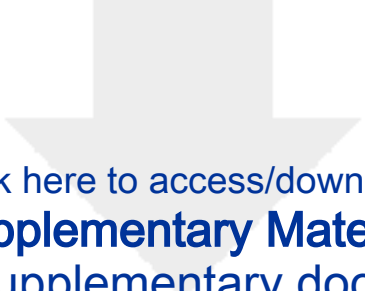
Table 1. Elemental analysis (atom %) of synthesized compounds.

Element	Si	O	C	N	W
SiO ₂ @SiC	36.14	40.97	18.30	4.59	-
NH ₂ -SiO ₂ @SiC	36.28	30.96	25.08	7.68	-
W- NH ₂ -SiO ₂ @SiC	32.16	31.14	20.50	7.42	8.78
N-W-NH ₂ -SiO ₂ @SiC	29.57	27.92	27.21	7.79	7.51
N-W-NH ₂ -SiO ₂	21.71	56.65	-	9.56	12.08

Table 2. Textural characterization of synthesized samples.

Sample	S_{BET} (m^2/g) ^a	Total Pore Volume (cm^3/g) ^b	Micropore Volume (cm^3/g) ^c	Mesopore Volume (cm^3/g)	Average Pore Diameter (nm) ^a	Content % ^c	
						Micropore	Mesopore
SiO ₂ @SiC	31.41	0.242	0.046	0.196	30.78	18.86	81.09
N-W-NH ₂ - SiO ₂ @SiC	94.42	0.511	0.039	0.472	21.64	7.63	92.36

^a were determined by using the BET theory, ^b was measured by BJH method, and ^c were evaluated by the t-plot method.



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