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Vanadium–Schiff base complex-functionalized SBA-15 as a heterogeneous catalyst: synthesis, characterization and application in pharmaceutical sulfoxidation of sulfids

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Abstract VO_2(picolinichydrazone) complex as a catalyst was stabilized on a SBA-15 mesoporous silica as a catalytic support by using (3-chloropropyl)triethoxysilane as a connector. SBA-15 is nanoporous and has a high ratio of surface area to volume. The immobilization of a metal–Schiff base complex to the surface area of SBA-15 can improve its catalytic effects by increasing the catalytic surface area. Unlike homogeneous catalysts, heterogeneous catalysts can be recovered and reused several times without any significant loss of catalytic activity. A vanadium–Schiff base complex-functionalized SBA-15 was synthesized by covalency connected by a pre-synthesised VO_2(picolinichydrazone) complex to silanated SBA-15. The synthesized vanadium–Schiff base complex was characterized by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy and Fourier transform infrared spectroscopy (FT-IR), and the final V/SBA-15 was characterized by FT-IR, ultraviolet–visible spectrophotometry and X-ray powder diffraction. The morphology of V/SBA-15 was also obtained by scanning electron microscopy and transmission electron microscopy. The catalytic effect was examined by using V/SBA-15 as a heterogeneous catalyst in sulfoxidation reactions. The synthesis of modafinil and modafinic acid by pharmaceutical sulfoxidation of solfides was carried out and the effects of different solvents, reaction times and also recoverability and reusability of the heterogeneous catalyst were investigated. This catalyst showed high yield of sulfide conversion, stability and recyclability in the sulfoxidation of sulfides.

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Keywords SBA-15 · Nanoporous silica · Heterogeneous catalyst · VO_2(picolinichydrazone) complex · Modafinil · Modafinic acid

Introduction

Heterogeneous catalysts are used in all the chemical and biological transformations fields and play an important role in the world economy. Catalysis in biological systems is mainly managed by enzymes while in non-biological systems is carried out by reactive materials or transition metal catalysts, which can be used either homogeneously or heterogeneously. Although, homogeneous catalysts in comparison with heterogeneous catalysts have some important advantages such as high activity and high selectivity, their weak isolation and recovery need expensive processes and difficult conditions such as high-temperature distillations and high-volume extractions, which have limited its scale-up application [1, 2]. The dispersion and stabilization of metal catalysts on the surface of mesoporous particles can solve the recovery problem, while keeping its high activity and high selectivity due to large surface areas. Functionalized mesoporous materials such as mesoporous silica have become subjects of the most necessary advanced research fields of functional materials. They have wide range of applications in many areas such as catalysis [3, 4]. The synthesis of mesoporous silicas was suggested for the first time in 1992 [5] and, since then, considerable progress has been made in the morphology and pore size regulation and application developments of various types of mesoporous silica [6–8]. SBA (Santa Barbara Amorphous), is one of the different ordered and most studied mesoporous silicas [9–12]. The thick rim that can be easily functionalized using simple silanol chemistry has made the SBA-15 the best candidate as catalytic support [13] SBA-15 is a more interesting structure as catalyst support due to the mentioned properties, such as large surface areas and equal pore sizes [11, 12, 14]. In a similar field, vanadium–Schiff base complexes based on silica [15] and zeolite support [16] in the presence of H_2O_2 have been used as heterogeneous catalysts for the sulfoxidation of sulfides with high yields. Also, they are used as catalysts in the synthesis of numerous intermediate sulfur-containing drugs such as modafinil and modafinic acid which are used for the treatment of narcolepsy [17]. Schiff base complexes are very effective catalysts [18] and Schiff base ligands can be easily synthesized from the reaction of an aldehyde or ketone with an amine. The complexes of metal-coordinated Schiff base ligands are suitable for many applications such as chemical analysis [19], absorption of oxygen [20], n the remedy of cancers [21], in pesticides [22] and as catalysts [23–25].

In this study, the complexes of a Schiff base ligand and vanadium was synthesized and introduced to the silane-functionalized SBA-15 to act as a heterogeneous catalyst. Vanadium–Schiff base complex-functionalized SBA-15 was characterized by FT-IR, H NMR, C NMR, UV–Vis, XRD and TEM, and its catalytic effects were examined by sulfoxidation of sulfides for the synthesis of modafinil and modafinic acid drugs.

Materials and methods

Reagents

All the chemicals used in this work were analytical grade reagents and used without further purification. Deionized water was used to prepare all solutions.

Apparatus

The FT-IR analyses were carried out on a UniCam Matson1000FT-IR spectrophotometer using a K-Br pellet for sample preparation. 500 MHz ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker FT-NMR spectrometer. X-ray diffraction patterns (XRD) were collected using a Philips X'Pert MPDX-ray diffractometer equipped with a graphite monochromator, operating at 40 kV and 40 mA and employing Cu-Kα radiation ($\lambda = 1.54056$ Å). Scanning electron microscopy (SEM) was recorded by a Hitachi s4160 microscope operating at 15 kV. Transmission electron microscopy (TEM) was recorded by a JEOL 2010 electron microscope operating at 200 kV. Gas chromatography (GC) was recorded by a Chromatograph Agilent Technologies-6890 N using a 19091J-236 HP-5, 5 % phenyl methyl siloxane, with a 60 m × 250 μm × 1 μm capillary column.

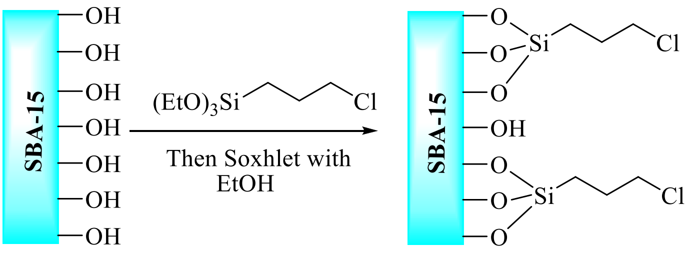
Preparation of the catalyst

Preparation of SBA-15 with 3-chloropropyltriethylsilane (CPTES)

The SBA-15 **1** was synthesized by a method reported in the literature [26]. In brief, 4.0 g of tri-block poly(ethylene glycol)-poly(propyleneglycol)–poly(ethylene glycol) (P123) was dissolved in a mixture of 30 ml deionized water and 120 ml HCl (2 mol/L) and stirred at 100 rpm at 40 °C for 12 h. Then, 8.14 ml of tetraethoxysilane (TEOS) and 2.04 mmol of 3-chloropropyltriethylsilane (CPTES) were added dropwise into the solution over 2 h and stirred for another 24 h at 40 °C. Then, the reaction mixture was placed in an autoclave for 24 h at 100 °C. Next, the mixture was filtered and the desired product was obtained as a yellow solid. The precipitate was washed with a mixture of ethanol and water (1:1), and dried at room temperature. The surfactant was removed using a soxhlet extraction system with ethanol for 3 days. The white solid of the functionalized SBA-15 **2** was dried for 24 h at 60 °C (Scheme 1).

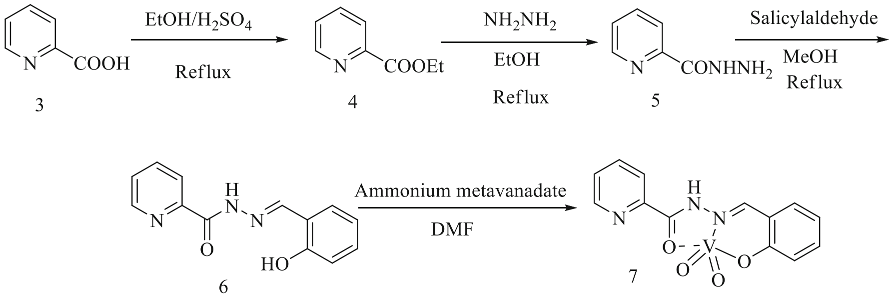
*Synthesis of the Schiff base ligand **6***

*Synthesis of ethyl picolinate **4*** To synthesize ethyl picolinate **4**, 6/61 g of picolinic acid **3** was dissolved in 70 ml of ethanol, and 10 ml of concentrated sulfuric acid was added dropwise. The reaction mixture was refluxed for 20 h. After completion of the reaction, the reaction mixture was cooled until reached pH = 8 with saturated Na_2CO_3. Finally, the organic phase was extracted with ethylacetate and the solvent was removed under vacuum. The yellow liquid was obtained in 83 % yield (Scheme 2).



1 2

Scheme 1 Functionalization of SBA-15 with CPTES



Scheme 2 Synthesis of dioxo vanadium-picolinichydrazone Schiff base complex **7**

Synthesis of the picolinohydrazide ***5*** Picolinohydrazide **5** was synthesized by the addition of a solution containing 50 mmol of hydrazine dissolved in 40 ml of ethanol to 10 mmol of ethyl picolinate **4** and refluxed for 10 h. Then, the volume of the solvent was reduced to 10 ml and cooled to room temperature when a white solid as the product was precipitated. The crude product was recrystallized in ethanol to obtain picolinohydrazide in a yield of 74 % [22] (Scheme 2).

Synthesis of the picolinichydrazine Schiff base ***6*** To synthesize picolinichydrazine Schiff base 6, 1 mmol of picolinohydrazide 5 was dissolved in 30 ml methanol and added dropwise to 1 mmol salicylaldehyde. The solution color changed to yellow immediately. The reaction mixture was refluxed for 3 h. After completion of the reaction, the solvent volume was reduced and cooled to room temperature to precipitate the crude product. The precipitate was filtered and washed with methanol and dried at room temperature when picolinichydrazine Schiff base was obtained in a yield of 89 % (Scheme 2).

Synthesis of the dioxo vanadium-picolinichydrazone Schiff base complex ***7***

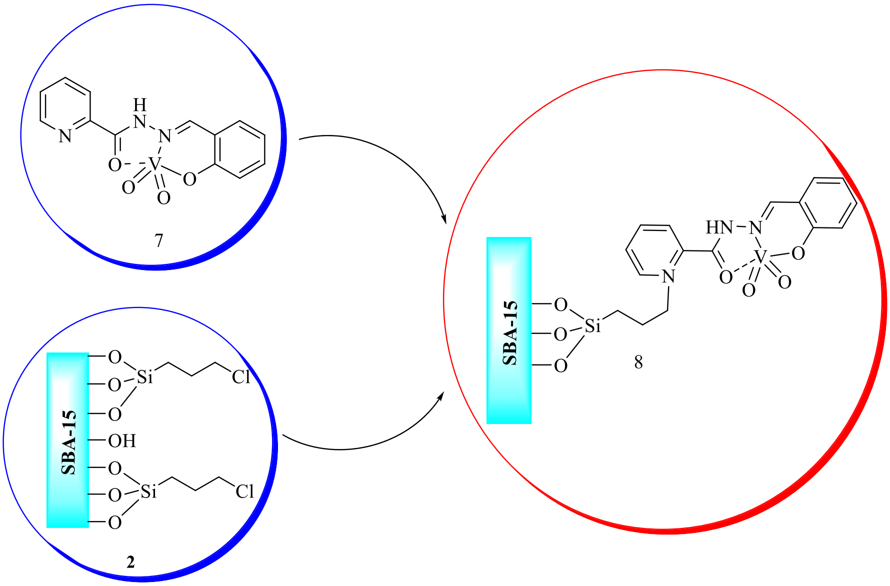
The dioxo vanadium-picolinic hydrazone Schiff base complex **7** was synthesized by dissolving of 1 mmol picolinic hydrazine Schiff base **6** in 40 ml of dimethylformamide and the addition of 1 mmol ammonium metavanadate (Scheme 2). After stirring the mixture for 30 min, the orange precipitate was filtered and washed with dimethylformamide and dried at room temperature (yield: 85 %). ^{1}H NMR[DMSO-d6, 500 MHz, δ (ppm)]:9/00 (s, 1H, CH = N), 8/71 (d, $J = 4/5$ Hz, 1H), 8/08 (d, $J = 7/8$ Hz, 1H), 7/95 (t, $J = 6/8$ Hz, 1H), 7/76 (dd, $J = 7/7$, 1/30 Hz, 1H), 7/57 (m, 2H), 7/10 (t, $J = 7/4$ Hz, 1H), 7/00 (d, $J = 8/2$ Hz, 1H), 4/09 (q, $J = 5/1$ Hz, 1H), 3/17 (d, $J = 5/1$ Hz, 1H). ^{13}C NMR[DMSO-d6, 500 MHz, δ (ppm)]:173/2, 168/5, 161/0, 150/1, 149/6, 138/1, 136/6, 135/4, 127/5, 124/8, 122/5, 121/0, 119/5.

Preparation of the heterogeneous catalyst

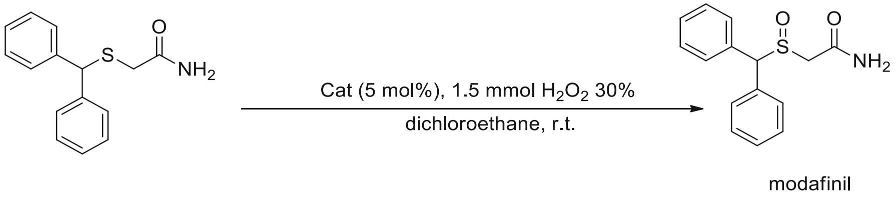
The V/SBA-15 **8** as a heterogeneous catalyst was synthesized by the dissolving of Cl/SBA-15 **2** (1 g) in 25 ml of dimethylformamide and its addition to 1 mmol of complex dioxo vanadium-picolinichydrazone **7**. The reaction mixture was stirred for 24 h at 80 °C. The solid was separated and washed with DMF several times and dried for 24 h at 60 °C (Scheme 3).

Catalytic experiments

To examine the catalytic activity of the heterogeneous catalyst, 1 mmol of sulfide, 1.5 ml of hydrogen peroxide 30 % as oxidant and 5 % mol of catalyst were dissolved in 3 ml solvent and reacted at room temperature for different times (Scheme 4; Table 1; Fig. 7). The monitoring of the sulfoxide formation was carried



Scheme 3 Preparation of V/SBA-15 **8**



Scheme 4 sulfoxidation of sulfides catalyzed by the V/SBA-15 for synthesis of modafinil drug

Table 1 Effect of solvent on the sulfoxidation of methyl phenyl sulfide using H_2O_2 catalyzed by V-SBA-15 at room temperature

Row	Solvent	Sulfoxide yield
1	CH_3CN	40
2	$C_2H_4Cl_2$	65
3	CH_2Cl_2	51
4	$C_2H_4Cl_2$	85
5	CH_3OH	46
6	CH_3CH_2OH	38

Reaction conditions: 5 %mol V/SBA-15,1 mmol thioanisole, 1.5 mmol H_2O_2 30 %, 3 ml solvent. Conversion sulfoxides monitored by GC method

out by TLC (n-hexanes:EtOAc, 1:1 or $CHCl_3$:MeOH, 9:1 as eluent). After completion of the reaction, the solvent was evaporated and the crude product was purified by a recrystallization method (using EtOAC/n-hexane) (Table 2). The catalyst was recovered and reused for further runs.

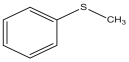
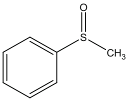
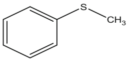
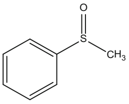
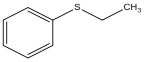
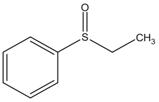
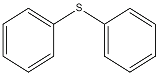
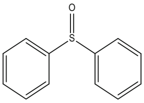
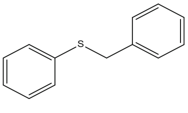
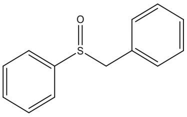
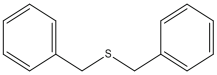
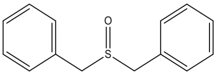
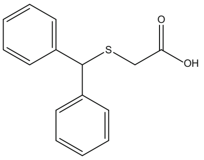
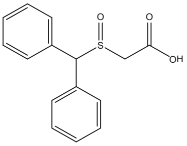
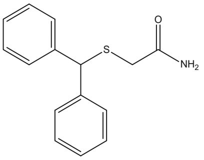
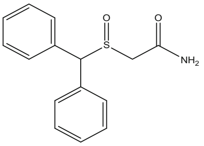
Results and discussion

Characterization methods

Low angle XRD patterns

XRD patterns of Cl/SBA-15 and VO_2(picolinichydrazone)/SBA-15, are shown for comparison in Fig. 1. In the diffraction pattern of Cl/SBA-15, three peaks are seen in θ_2 of 1/14, 1/88 and 2/13, respectively, corresponding to the reflection of 100, 110 and 200, which are related to an ordered structure with hexagonal (p6mm) symmetry [27]. The intensity of the diffraction peaks decreases by the complex stability on SBA-15. The gradual decline happens in the intensity of the peaks due to the loss of the regular structured SBA-15, which confirms the stabilization of the complex in the holes.

Table 2 Sulfoxidation of sulfide compounds with using hydrogen peroxide 5 mol % and V/SBA-15 catalyst

Entry	Sulfide	Product	Yield[a]
1			85
2			35[b]
3			80
4			70
5			89
6			94
7			91[c]
8			93[c]

[a] Reaction conditions: 5 % mol V/SBA-15,1 mmol substrate, 1.5 mmol H_2O_2 30 %, 3 ml solvent, reaction time 1.5 h and r.t. Conversion sulfoxides monitored by GC method

[b] Reaction conditions: 5 % mol V/SBA-15,1 mmol substrate, 2.5 mmol H_2O_2 30 %, 3 ml solvent, reaction time 1 h and at 40 °C. Conversion sulfoxides monitored by GC method

[c] Was determined by TLC (n-hexanes: EtOAc, 1:1) and using ICP-AES analysis

SEM image

Figure 2 illustrates the SEM image of V-SBA. The image indicates the morphology of the solid material containing a large number of worm-like areas with diameters of approximately 100–200 nm.

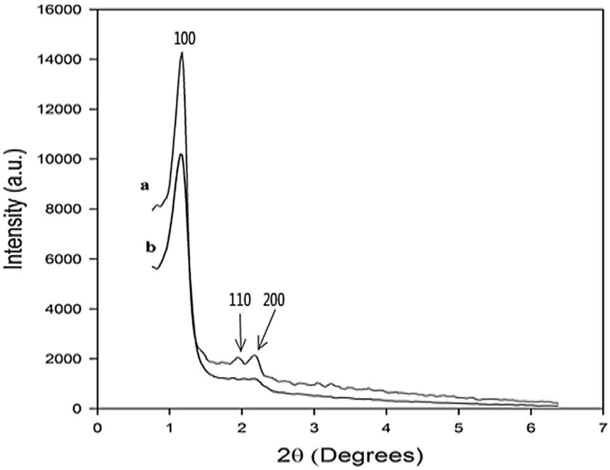
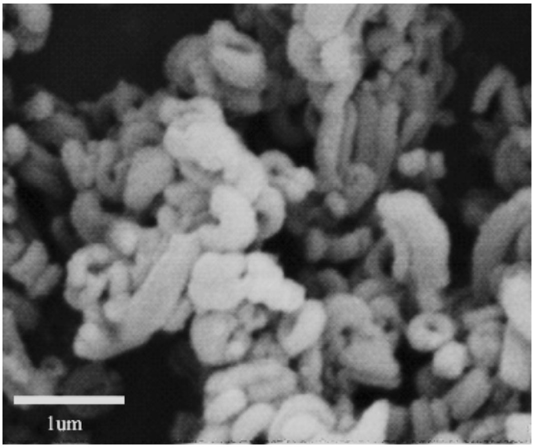


Fig. 1 XRD patterns of **a** Cl/SBA-15, **b** VO_2 (picolinichydrazone)/SBA-15

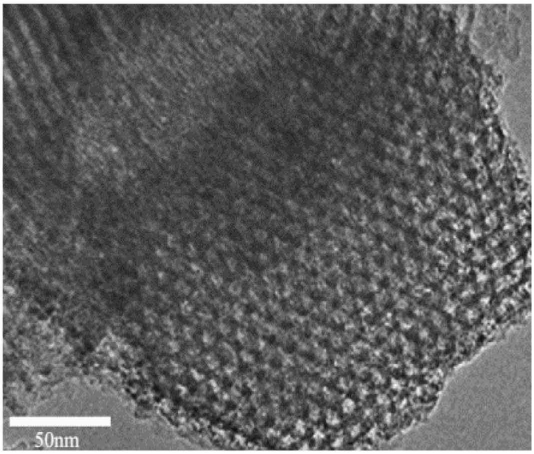
Fig. 2 SEM image of V-SBA



TEM image

The TEM image of V/SBA-15 is shown in Fig. 3 and confirms the very regular structure of the final heterogeneous catalyst. As shown, the catalyst has parallel channels with regular holes in hexagonal (P6mm) symmetry which is in accord with the XRD pattern. These results clearly show that, even though the molecule VO_2(picolinichydrazone) is inserted inside channels of SBA-15 functionalized by CPTES, the structural integrity was maintained.

Fig. 3 TEM image of V-SBA



Thermogravimetry analysis

Thermal gravimetric analysis (TGA) was performed to evaluate the thermal stability of VO_2(picolinichydrazone)/SBA-15. As shown in Fig. 4, the TGA diagram has three steps of weight loss, which gives the quantitative data for determining the loading complex. In the temperatures ranging from 0 to 110 °C, water and other solvents which were physically absorbed are eliminated [28]. In the range of 110–350 °C, the reducing weight is related to the desorption of the water which is chemically adsorbed on the silica surface [29]. Furthermore, extra decomposition from the residual surfactant occurs in this range [30]. The 3.52 % weight loss for VO_2(picolinichydrazone)/SBA-15 at 360–780 °C is attributed to the decomposition of the ligand and organic functional groups into the SBA-15 pores [31]. The weight losses of the VO_2(picolinichydrazone) complex in the third stage are 0.142 mmol/g of the sample.

Catalytic activity

The sulfoxidation of methyl phenyl sulfide was chosen to analyze the catalytic effects of VO_2(picolinichydrazone)/SBA-15 heterogeneous catalyst and optimize different conditions such as different times, solvents and catalyst content and recovery. At first, different solvents were used for the sulfoxidation reaction in catalytic conditions and at constant time. As shown in Table 1, the reaction that was carried in dichloroethane as a solvent had the highest yield in comparison with the other used solvents so that dichloroethane was chosen as the optimum solvent. At the second step, the sulfoxidation reaction was performed in constant catalytic conditions in the dichloroethane and the progress of the reaction was analyzed at different times. As shown in Fig. 7, sulfoxidation reaction of methyl phenyl sulfide takes 2 h for completion at room temperature. Also, at higher temperature and a higher concentration of H_2O_2, the reaction took place in a shorter time with oxidation and sulfone being formed (Table 2, entry 2).

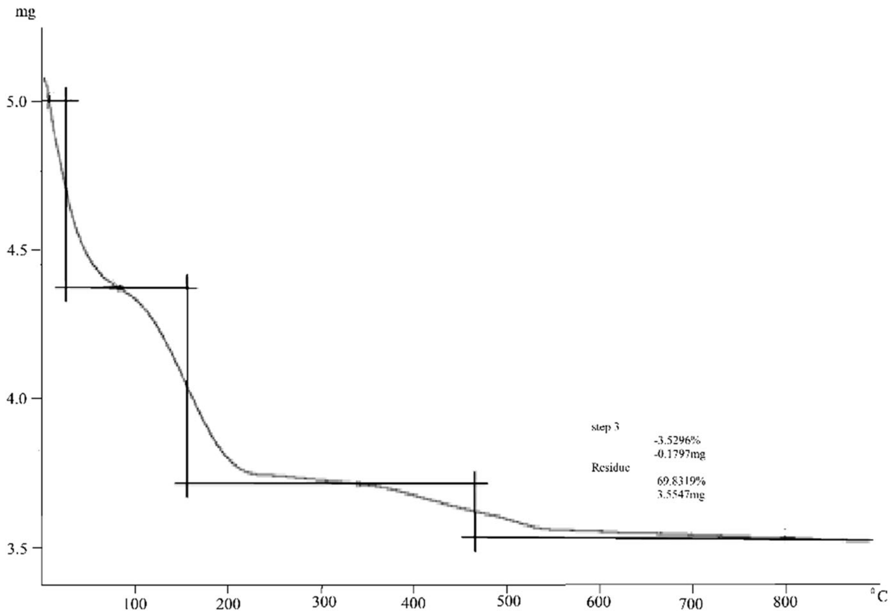


Fig. 4 TGA curve of V-SBA-15

Also, the effect of the sulfide structures on the sulfoxidation reaction under optimized catalytic conditions was investigated (Table 2). The oxidation of methyl phenyl sulfide (1 mmol) using 30 % H_2O_2 (1.5 equiv) and SBA-15/VO_2(picolinichydrazone) (5 mol %) in $C_2H_4Cl_2$ (3 mL) at room temperature was carried out in a short reaction time (1.5 h) and in high yield (%85) (Table 2, entry 1).

In a blank experiment, and in the absence of SBA-15/VO_2(picolinichydrazone), no considerable oxidation was observed under the same reaction time and similar reaction conditions. The blank reaction neede 24 h to reach a reasonable conversion.

In a similar way, various types of structurally different aryl alkyl sulfides underwent oxidation reaction under similar conditions and produced corresponding sulfoxides in good to excellent yields (Fig. 2, entries 3–5). It has been previously shown that the formation of sulfoxides from diaryl sulfides under standard oxidation procedures by using 30 % H_2O_2 is difficult [32]. But, interestingly, under the described reaction conditions, diaryl sulfides produced corresponding sulfoxides in good to excellent yields (entry 4)

FT-IR and UV–Vis

The FT-IR spectra of Cl/SBA-15, VO_2(picolinichydrazone) and VO_2(picolinichydrazone)/SBA-15 are shown in Fig. 5 for comparison. The peak appearing at 1637 cm^{-1} in the spectrum of Cl/SBA-15 is related to the O–H bending vibration of H_2O. The peak appearing at 3440 cm^{-1} is related to the stretching vibration O–H bonds and the peaks appearing at 803 and 1074 cm^{-1} are assigned to the stretching

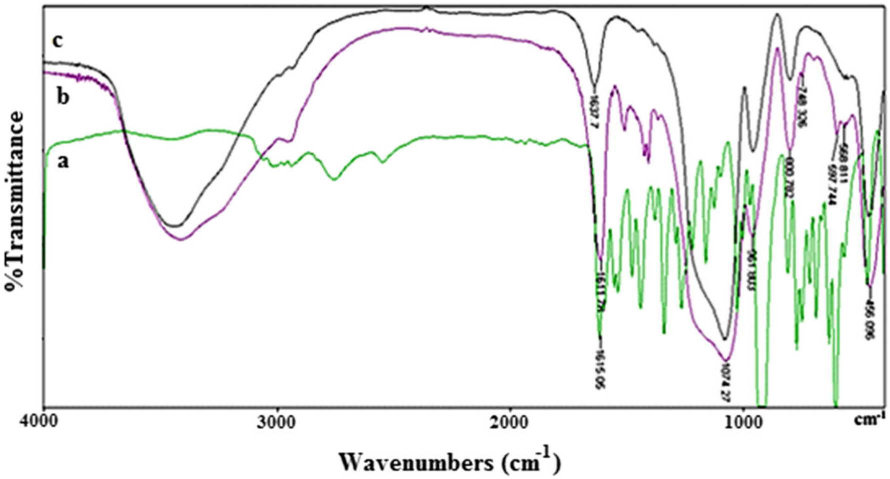


Fig. 5 FT-IR **a** VO_2(picolinichydrazone), **b** VO_2(picolinichydrazone)/SBA-15, **c** Cl/SBA-15

vibration of symmetric and asymmetric Si–O–Si bonds. In the spectra of VO_2(picolinichydrazone)/SBA-15 and Cl/SBA-15, bands at 958 and 459 cm^{-1} correspond to Si–O stretching vibration in the Si–OH groups and Si–O–Si bending vibration, respectively, which is evidence for the formation of a silica network. As can be seen, the bands of VO_2(picolinichydrazone)/SBA-15 have a low intensity in comparison with the VO_2(picolinichydrazone) peaks. This is due to the low concentration of the pores which have stabilized. Because of the stabilizing effect of the complex on the SBA-15, the band of stretching vibration of the C=N bond in the complex shifts from 1615 to 1611 cm^{-1}. Also, the peaks at 1557, 1537, 1480 and 1444 cm^{-1} are shifted to 1512, 1508, 1422 and 1406 cm^{-1}, respectively. This shift in absorption bands can be attributed to the changing of the geometric configuration of the complex in the SBA-15 pores.

UV–vis spectra of VO_2(picolinichydrazone)/SBA-15 and complex VO_2(picolinichydrazone) are shown in Fig. 6. By comparing the absorptions, a blue shift in bands due to the stabilization in the pores can be observed. The LMCT band at 400 nm has not moved but the intensity has been reduced due to the complex stabilizing on the surface.

(Figs. 5, 6, 7).

The narcolepsy drugs, modafinic acid and modafinil, were also synthesized by using vanadium-based catalytic systems (Table 2, entries 7 and 8). The results show high yields of reactions for modafinic acid and modafinil (91 and 93 %, respectively) in short reaction times (1.5 h). According to the results, it has been demonstrated that, in optimized conditions, the VO_2–Schiff base complex stabilized on SBA-15 is one of the best candidates for the synthesis of modafinil.

According to the suggested mechanism shown in Scheme 5 [33], by increasing the nucleophilic effect of the sulfur atom on the vanadium catalyst, the yield of sulfoxidation is increased.

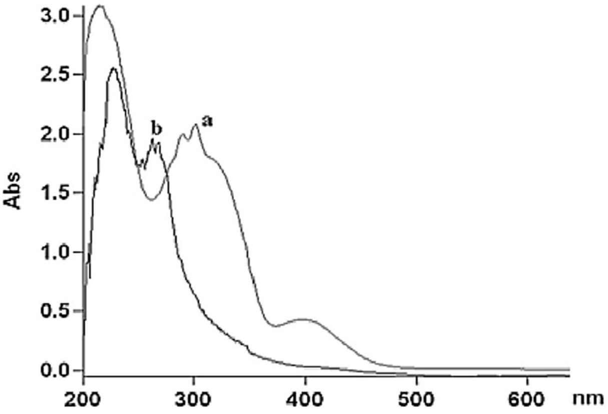


Fig. 6 UV–Vis spectra of **a** VO_2(picolinichydrazone)and **b** SBA-15/VO_2(picolinichydrazone)

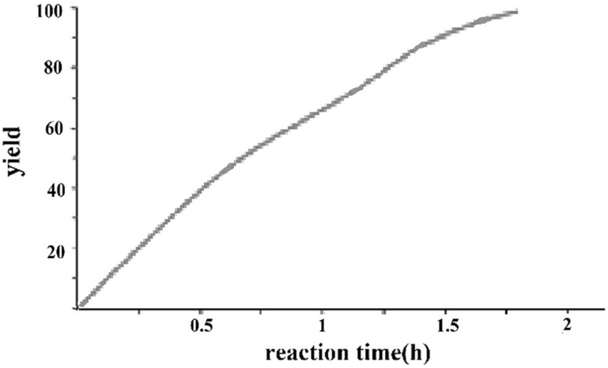
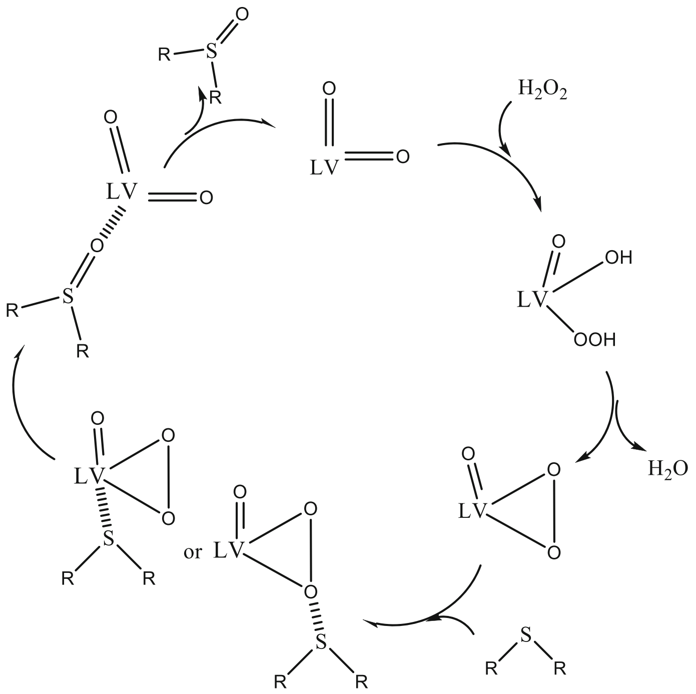


Fig. 7 Effect of time on the sulfoxidation of methyl phenyl sulfide using H_2O_2 catalyzed by V-SBA-15 at room temperature

The recyclability of the modified catalyst was investigated by reusing the catalyst isolated from a previous run in the next run of sulfoxidation of methyl phenyl sulfide under the same conditions. For the reusability reaction, the catalyst was isolated from the reaction solution after the complete sulfoxidation of methyl phenyl sulfide by simple filtration, washed with dichloroethane, and dried at room temperature. Further, the resulting filtrate was investigated by AAS analysis which suggested that negligible leaching of the vanadium ions was observed during each run which confirmed that the catalyst is heterogeneous. In the sulfoxidation of methyl phenyl sulfide, slowing down of the reaction was observed in the recycling runs (four runs), although conversion in all cases remained very high (Table 3).

The effect of catalyst amount was evaluated and the results are reported in Fig. 8. Without a catalyst, the reaction occurred under the conditions reported in Fig. 8 to give 11 % yield. Active sites on the porous surface of the catalyst were considerably increased by adding the catalyst and reached the best yield value (85 %) with 5 %



Scheme 5 Suggested mechanism for the oxidation of sulfides with the catalyst V/SBA-15

Table 3 The recovery results of the V/SBA-15 catalyst and the leaching of the catalyst per cycle in the sulfoxidation reactions by using hydrogen peroxide as oxidant

V/SBA-15	Vanadium content (wt%)	Yield
Fresh	3.00	85
I cycle	2.81	80
II cycle	2.73	77
III cycle	2.10	69

Reactiuons conditions: 5 %mol V/SBA-15,1 mmol substrate, 1.5 mmol H_2O_2 30 %, 3 ml solvent, reaction time 1.5 h

mol of V/SBA-15 catalyst with respect to the thioanisole. Further increasing of the catalyst amount did not lead to a substantial increase in conversion.

Conclusion

The Schiff base complexes have catalytic features, and one of the best Schiff base complexes that shows the best catalytic properties is VO_2(picolinichydrazone). In this study, VO_2(picolinichydrazone) complex was established onto functionalized

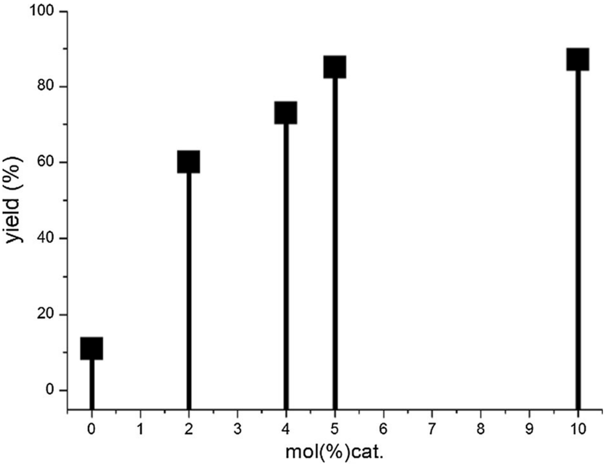


Fig. 8 Effect of catalyst amount on oxidation of thioanisol. Reaction conditions: thioanisole (1 mmol), 1.5 mmol H_2O_2 30 %, 3 ml $C_2H_4Cl_2$ as solvent, reaction time 1.5 h, r.t

SBA-15 to act as a heterogeneous catalyst. The bond between the support and the complex was so strong that it was not removed by water or solvents. The heterogeneous VO_2(picolinichydrazone) catalyst was especially applied in the pharmaceutical synthesis of modafinil and modafinic acid and gave higher yields in the sulfoxidation reactions. This heterogeneous VO_2(picolinichydrazone) catalyst is stable and can be recycled in the sulfoxidation of sulfides.

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