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Application of Silica vanadic acid as a heterogeneous, selective and highly reusable catalyst for oxidation of Sulfides at room temperature

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Highlights

Application of supported transition metal oxides catalyst Using catalyst in large scale High reusable catalyst Chemoselectivity and homoselectivity High TON and TOF

Abstract

Silica vanadic acid (Vanadium has been supported on silica) is applied as an efficient, highly reusable and heterogeneous catalyst for the selective oxidation of sulfide to sulfoxide using hydrogen peroxide and in the acetonitrile as a solvent at room temperature. The catalyst can be easily recovered and reused for ten reaction cycles without considerable loss of activity. Also,

some advantages of this method were applicable at large scales, high TON of catalyst, chemoselectivity, easy work-up and short reaction time.

Keywords: Silica vanadic acid, hydrogen peroxide, heterogeneous, large scales, chemoselectivity, highly reusable catalyst.

1. Introduction

In recent years, considerable emphasis has been placed on improvement in the environmental impact of industrial chemical processes. Thus, green chemistry has been defined as a set of principles which reduce or eliminate the use or generation of hazardous substances and catalysts throughout the entire life of chemical materials. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research. The inherent advantages of heterogeneous catalyst system in liquid phase over their homogeneous counterparts lie mainly on their easy separation and recycling ability as well as minimization of undesired toxic wastes. These types of catalysts have used various support materials. One useful example of support materials is Silica gel. This inorganic supporter has some advantageous properties such as excellent stability, good accessibility and high surface area which will be beneficial to the enhancement of loading amount and dispersion of catalytic active [1].

Oxidation over metal catalysts using eco-friendly oxidants such as hydrogen peroxide and molecular oxygen are preferred for environmental and economical benefits. Along this line, the design of soluble and heterogenized metal catalysts represents a rapidly growing field that has been significantly applied in industry. Among the various transition metals, vanadium, an early member of the3d transition metal series, exists on the surface of the earth more abundantly and vanadium-based oxidants are effectively used for various oxidation reactions such as methanol oxidation, carbon monoxide oxidation and partial oxidation of hydrocarbons. Also, supported

vanadium oxides constitute a very important group of catalysts that are industrially used for sulfuric acid manufacture, oxidation of o-xylene to phthalic anhydride, ammoxidation of alkyl aromatics to aromatic nitriles, and the selective catalytic reduction (SCR) of NOx emissions with NH_3 to N_2 [2-5].

Sulfides oxidation is one of the most important organic processes, since the corresponding sulfoxides are valuable synthetic intermediates for the synthesis of chemically and biologicallyimportant molecules [5-7]. Sulfoxides are also valuable in the C–C bond-formation [8] and molecular rearrangements [9,10]. Additionally, some of the biologically active sulfoxides play important roles as therapeutic agents such as anti-ulcer [11,12], antibacterial [13] etc. Although sulfides can be easily oxidized by wide variety of oxidizing reagents [14-24], unfortunately, some of these reagents are not satisfactory for the selective oxidation of sulfides to the sulfoxides because of several reasons such as over oxidation to sulfones, low selectivity, low yields of products, long reaction time, high temperature, large amount of reagent and expensive reagents or catalysts.

Aqueous hydrogen peroxide is a well known oxidant because it is a cheap, mild and environmentally acceptable reagent with a high content of active oxygen and produces water as a by-product [25]. Moreover, oxidation over metal support catalysts using eco-friendly oxidants such as hydrogen peroxide and molecular oxygen is preferred now for environmental and economical benefits [26].

In continuation of our ongoing research program on the applications of heterogeneous and silica supported transition metal oxides catalysts for oxidation of organic functional groups [27-32], we found that Aboelfetoh and Pietschnig react vanadiumoxytrichloride (**I**) with silica gel to give silica vanadic acid (SVA) (**III**) during an easy and clean reaction [33]. VOCl₃ (**I**) is a powerful

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oxidizing agent [34-36] but many of the reported methods in which it has been used as catalyst or reagent are associated with one or more of the following drawbacks: (i) toxicity of VOCl₃ (ii), production of harmful HCl, (iii) by-products formation, (iv) harsh reaction conditions, and (v) no agreement with the green chemistry protocols. However, when vanadiumoxytrichloride is supported on a silica gel (silica vanadic acid), it is easy to be applied as a catalyst or reagent in reactions (Figure 1).



Scheme 1. Synthesis of Silica Vanadic Acid (SVA)



Figure 1. Vanadiumoxytrichloride (**I**), (**B**) silica-supported vanadiumoxy dichloride (deep red) (**II**), (**C**) Silica Vanadic Acid (deep green) (**III**).

Thus, in our present work, we were interested in using SVA to promote oxidation of sulfides with H₂O₂ (Scheme 2).



Scheme 2. Oxidation of sulfides using SVA/H₂O₂ in CH₃CN as solvent at room temperature

2. Experimental

2.1. Materials

All the sulfide substrates and VOCl₃ were obtained from Aldrich, merck, alfa-aser and used as received without any further purification.

2.2. Synthesis of silica vanadic acid

In a 100 ml round-bottomed flask, *n*-hexane (25 mL) and silica gel (4.0 g) were stirred for 10 min and then vanadiumoxytrichloride (4.0 g) was dissolved in n-hexane (25 mL) and added drop wise to silica gel suspension (15-20 min). After addition of VOCl₃, the red-brown mixture was stirred for 10 hours. Then, solvent was evaporated and the residue (the red-brown powder (**II**) obtained after the grafting process) was filtered, washed with dry *n*-hexane several times to remove unreacted VOCl₃, dried under vacuum, and stirred in the air for 72 hours to promote the hydrolysis of V–O–Cl bonds [33, 37]. At this time, the red-brown powder changed to dark green powder (**III**) slowly (Scheme 1). Typical loading of Vanadium was determined using X-ray fluorescence (XRF) and shows a loading $8 \pm 0.1 \text{ mmol g}^{-1}$.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of all catalysts were performed on a APD 2000, Ital structure with Cu Ka radiation (k = 0.1542 nm) operating at 50 kV and 20 mA in a 2h range of 10–70° with step size 0.01_o and time step 1.0 s to assess the crystallinity of the vanadium oxide loading. The vanadium concentration of the prepared catalysts was determined by XRF ARL8410.

Fourier transform-infrared spectra of the samples were recorded on a Perkin–Elmer FT-IR spectrometer 17259 using KBr disks. Thermogravimetric analyses using a Perkin–Elmer TGA were performed on both support materials (II and III) and all prepared catalysts. To evaluate the overall amount of surface hydroxyl groups available for anchoring reactions, the weight loss

between 300 and 600 oC was determined. A heating rate of 10 ^oC/min under argon was applied to purge off-gasses from the TGA electronics and sample region. Semi-quantitative EDX (Ro[°]ntec, Quantax/QX2) analysis was used for the characterization of element concentration and vanadium distribution within prepared catalysts. The SEM analyses were done with a TESCAN/VEGA with a maximum acceleration voltage of the primary electrons between 10 and 15 kV.

The IR Spectra of catalyst showed some peaks in region of 471, 800, 1097, 1632 and 3415 cm⁻¹. The band of the V–O–Si rocking vibrations appears about 471 cm⁻¹ [38]. The band at 800 cm⁻¹ is assigned to symmetric vibrations (Si–O–Si) and the band at 1097 cm⁻¹ is assigned to the asymmetric vibrations of (Si–O–Si) of silica vanadic acid [39]. The silica impregnated catalyst with high V loading exhibit a very weak band at 973 cm⁻¹, which indicates an asymmetric stretching mode of Si–O–V [33].



Figure 2. IR Spectra of catalyst

The morphology of the silica vanadic acid was observed using an SEM. Typical SEM images are shown in (Figure 3).



Figure 3. SEM image of catalyst

The XRD patterns of catalysts show partially amorphous nature of silica Fig. 4a. In the EDS spectrum of the as-synthesized sample, the peaks of Si and V are obviously observed, and no other impurities occur (Fig. 4b).



Figure 4. (a). XRD of catalyst, (b). EDS spectra of silica vanadic acid

Thermal analysis of the samples gives information about the stability of the $-VO(OH)_2$ groups. In the TG/DTG curve of catalyst, the weight loss below 120°C (<15%) is due to the desorption of water. Analysis of these diagrams strongly proposed that silica vanadic acid structure was stable and no further weight loss occurs below 210 $^{\circ}$ C. Decomposition of the vanadic acid groups takes place below 400°C (Fig.5).



Figure.5 TGA and and DTG of catalyst.

2.4. Oxidation of benzyl phenyl sulfide to benzyl phenyl sulfoxide

A mixture of benzyl phenyl sulfide (1 g, 5.0 mmol), silica vanadic acid (5mg, 0.039 mmol of V) and H_2O_2 30% (6 mmol) in CH₃CN (3 mL) was stirred for 10 min. After completion of the reaction, solvent was evaporated and the product was extracted with ether (2×10 mL), dried with anhydrous Na₂SO₄, filtered and evaporated to afford the crude sulfoxide product. Finally, the product was purified by column chromatography using ethyl acetate/hexane (1.5:8.5) as eluent to give benzyl phenyl sulfoxide as a white solid in 93% yield.

2.5. General procedure for the oxidation of sulfide to sulfoxide in large scale

A mixture of sulfide (50 mmol), silica vanadic acid (50mg, 0.39 mmol of V) in CH₃CN (30 mL) was stirred at room temperature for 5 min. Then, the solution of H_2O_2 30% (60 mmol) was added dropwise (15-20 min). After completion of reaction, solvent was evaporated and the product was extracted with ether (3×20 mL) dried with anhydrous Na₂SO₄, filtered and evaporated to afford the crude sulfoxide product. Finally, the product was purified by column chromatography using ethyl acetate/hexane (1.5:8.5) as eluent to give benzyl phenyl sulfoxide as a white solid in 86% yield.

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3. Result and discussion

3.1. Catalytic activity

In the beginning, conversion of benzyl phenyl sulfide into its corresponding benzyl phenyl sulfoxide has been considered as a model reaction. Different reaction parameters such as amount of catalyst, nature of solvent and type of oxidant are studied.

First of all, the reaction of benzyl phenyl sulfide was tested using different amounts of silica vanadic acid at room temperature (Table 1). As it can be seen in table 1, the best amount of the catalyst was 0.005 gr.

Solvent has a significant effect on the reaction even though the exact role of the solvent is not very clear. We carried out the reaction with the same concentration of the reactants in H_2O , MeOH, THF, CH₃CN and CH₂Cl₂. Both the yields and the reaction times listed in Table 1, suggest that acetonitrile appears to be the most suitable solvent for the oxidation reaction (Table 1, entries 4, 7-10). However, it is known that acetonitrile also activates H_2O_2 by forming an intermediate which is a good oxygen transfer agent [40].

Table 1. The reaction of benzyl phenyl sulfide with Hydrogen peroxide using different amounts of catalyst in various solvent^a

Entry	mmol of	Solvent	Amount of Catalyst Mol%	Time(h)	Yield(%) ^b
	sulfide		(g)		
1	5 mmol	CH ₃ CN		5	sluggish
2	5 mmol	CH ₃ CN	0.16 Mol%(0.001)	5	55
3	5 mmol	CH ₃ CN	0.48 Mol%(0.003)	1.5	88
4	5 mmol	CH ₃ CN	0.8 Mol%(0.005)	10(min)	94
5	5 mmol	CH ₃ CN	1.6 Mol%(0.01)	10(min)	92
6	5 mmol	CH ₃ CN	8 Mol%(0.05)	10(min)	93
7	5 mmol	THF	0.8 Mol%(0.005)	5	75
8	5 mmol	H_2O	0.8 Mol%(0.005)	5	25
9	5 mmol	CH_2Cl_2	0.8 Mol%(0.005)	5	50
10	5 mmol	CH ₃ OH	0.8 Mol%(0.005)	1	

^a Reaction Condition: sulfide (5 mmol), H₂O₂ (6 mmol), solvent, room temperature, stir. ^b Isolated

Yields, ^c Mixture of sulfoxide and sulfone.

In order to understand the preferred catalyst to other vanadium (V) compounds, benzyl phenyl sulfide was treated with ammonium vanadate 5% and 10% under optimum reaction conditions instead of SVA as a catalyst (Table 2). We found that in these circumstances the mixture of sulfone and sulfoxide produced and the reaction time is increased. Therefore, these modified silica gel catalysts enhance not only the conversion of organic sulfides but also the selectivity towards the formation of sulfoxide.

Table 2. Catalytic activity of different vanadiume (V) oxide on the reaction of benzyl phenyl sulfide and H_2O_2 (30%) in acetonitrile at room temperature.

Entry	Catalyst	Catalyst amount (Mol%)	Time (min)	Yield (%)	-
1	Silica Vanadic Acid	0.8	10	93 ^a	
2	NH_4VO_3	5	90	b	
3	NH ₄ VO ₃	10	75	_b	
8 T 1	1 x r · 1 1 h · · · 0 10	1 1 10			-

^a Isolated Yields, ^b mixture of sulfoxide and sulfone

3.2. The effect of different oxidant

In the next experiment, we examined the effect of various oxidants in the efficiency of the reaction, carried out in the presence of hydrogen peroxide, urea hydrogen peroxide (UHP), sodium perborate and sodium per carbonate as oxidant. In the absence of oxidant, the oxidation reaction was failed. As shown in figure 6, a maximum conversion take as place for H₂O₂ followed by sodium per carbonate (Na₂CO₃. 1.5H₂O₂) whereas sodium perborate (Na_BO₃.4H₂O) and urea hydrogen peroxide (UHP) are not found to be effective for the oxidation even after 18 hours (Fig. 6). The conversion percentage of sodium per carbonate is almost similar to that of hydrogen peroxide but the reaction with sodium per carbonate was completed after 16 hours while reaction time in hydrogen peroxide was 10 minutes. At a higher concentration of hydrogen

peroxide (2.5 equiv.), the reaction took place at a shorter reaction time (5min) with over oxidation and sulfone was formed.



Figure 6. Effect of the nature of the oxidant on benzyl phenyl sulfide conversion to benzyl phenyl sulfoxide (6 mmol oxidant. Other reaction conditions same as that for table 1).

3.3. Generality, Chemoselectivity, Homoselectivity and catalyst reuse

To assess generality and efficacy of the method, different aromatic, linear and cyclic aliphatic sulfides were reacted with hydrogen peroxide 30% in the presence of silica vanadic acid and CH₃CN as solvent under the optimized reaction conditions. The respective results are summarized in Table 3. As it can be seen in Table 3, the protocol was general and efficient. All reactions proceeded efficiently and the desired products were obtained in good to excellent yields in relatively short reaction times. Also, to show the chemoselectivity of the described system, three sulfides containing a hydroxy group were subjected to the sulfoxidation reaction, but alcohol oxidation did not occur under the mentioned conditions, and primary hydroxyl group remained intact in the course of the reaction (Table 3, **2f**, **2g** and **2h**, Scheme 3).



Scheme 3. Chemoselective sulfoxidation of 2-(phenylthio) ethanol and 2-(metylthio) ethanol. It is of interest to note that the mentioned oxidizing system allowed the homoselective [41,42] oxidation of bis-(methyl thio)-methane to their monosulfoxide derivatives (Scheme 4, Table 3, 2i).



Scheme 4. Homoselective oxidation of bis-(methyl thio)-methane to corresponding monosulfoxide derivative.

Table 3. Oxidation of sulfides 1 to the corresponding sulfoxides 2 using H2O2(30%) and catalytic amounts of silica vanadic acid (III) in acetonitrile at roomtemperature^a

Entry	Substrate (1)	Product (2)	Time (min)	Yield(%) ^b	
а	S S		10	93	
b	S_S		13	91	
с	SMe	O S Me	5	94	
d	S	O S S	40	88	
e	~~~s~~~~		20	89	
f	ССССОН	он Состатория Состатори Состатори Состатори Состатория Состатория Состатори	25	91°	
g	∕ ^S ∕∕OH	O S OH	20	90°	0
h	СІ	С	25	93°	a
i	_SS_	O S S S S	30	87 ^c	
j	o s	o s=0	15	92	
k	SOMe	O S O Me	25	94	

Reaction Condition: sulfide (5 mmol), H₂O₂ (6 mmol), solvent, room temperature, stir. ^b Isolated Yield. ^c Reaction Condition: sulfide (1 mmol) , H₂O₂ (1.2 mmol), solvent (3 mL), room temperature, stir.

In order to recover the catalyst, CH₃CN was evaporated under the reduced pressure and removing the product by extracting with ether from the reaction mixture and charging the reaction vessel with fresh substrate and H₂O₂ 30% and then repeating the experiment. The recovered catalyst was reused ten times in the oxidation of benzyl phenyl sulfide (**1a**) with H₂O₂, and smooth loss of catalytic activity was observed from the 7th time of reuse (Fig. 7).



Figure 7. The catalytic activity of SVA in ten cycles for the reaction of benzyl phenyl sulfide (1a) with Hydrogen peroxide.

3.4. Comparison with other reported methods

To assess the capability and efficiency of our catalyst with respect to the reported catalysts for oxidation of sulfide, the results of the application of these catalysts for the preparation of some sulfoxides are tabulated in Table 4. As shown in Table 4, higher yield and shorter reaction time were obtained using silica vanadic acid. Furthermore, we calculated turn over numbers (TON) and turn over frequencies (TOF) states on the effectiveness of these catalysts for the oxidation of sulfide to sulfoxide (Table 4). The TON and TOF values showed that SVA is more effective than another reported catalyst.

 Table 4. Comparison of the oxidation of benzyl phenyl sulfide (1a) with H2O2 (30%) using the reported catalysts

 versus Silica Vandic Acid.

Entry	Catalyst	Mol%	$\mathrm{H}_{2}\mathrm{O}_{2}$	Time	Yield (%) ^a	TON ^b	$TOF^{c}(min^{-1})$
			(mmol)	(min)			
1	Silica Vandic Acid	0.8	1.2	10	93 [This Work]	116.25	11.625
2	Silica-Based Tungstate	1	3	180	83[45]	83	0.46
3	$ZrCl_4$	 ^f	14	2	96[44]	0.24	0.12
4	Ta(Cl) ₅	2	5	120	95[48]	47.5	0.39
5	HCl	10	8	300	91[43]	0.91	0.003
6	Cu(II)	1	10	1200	52[45]	52	0.043
7	Mn(III)	1	8	19	84 [47]	84	4.42
8	Ce(OTf) ₄ ·xH ₂ O	5 ^e	3 ^d	360	94[50]		
9	TiO ₂	2.5 ^e	2.5	160	80 [49]		

^a Isolated Yield, ^b Turn over number, ^c Turn over frequency, ^dH₂O₂ (50%), ^e mg, ^f Condition: ZrCl₄ (4mmol), sulfide 1 mmol.

3.5. Oxidation of sulfide to sulfoxide in large scale

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In another study, to recognize the applicability of our method at large scales, we examined some reactions in scales of 10 and 50 mmol. The results are summarized in Table 5. As shown in Table 5, the reactions were successfully performed at large scales without significant loss of the yields.

Amount of substrate/mmol	product	Time (min)	Yield (%) ^a
5	2b	13	91
10	2b	20	90
50	2b	25	86
5	2c	5	94
10	2c	10	92
50	2c	15	90
5	2d	40	88
10	2d	50	85
50	2d	85	81

2e

Table 5. The large scale oxidation of sulfides using SVA/H2O2/CH3CN at room temperature

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10	2e	25	88
50	2e	35	85

^a Isolated Yield

3.6. Reaction mechanism

Based on a variety of studies, a mechanism as depicted in Fig. 8 has been proposed [51]. The catalytic cycle involves, as fundamental step, the formation in the active site of a peroxovanadium species (IV) [49, 50, 51], which is a much stronger oxidant than H2O2 [52]. The peroxoderivative oxidizes the sulfides to sulfoxide [53, 54, 55].



Figure 8. Proposed reaction mechanism

In conclusion, we have shown that the silica-based vanadium catalyst III can be easily prepared from commercially available materials. This catalyst efficiently affects the selective oxidation of a variety of sulfides to sulfoxides in room temperature with excellent yields without employing any co-reductant or other additives. The catalyst (III) can be considered as a heterogeneous version of VOCl₃. Therefore it is possible to easily recover and reuse for several reaction cycles without considerable loss of activity. The described method has many advantages, such as, chemoselectivity, easy work-up, short reaction time, high TON of catalyst and applicability of this method at large scales.

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Graphical Abstract

Application of Silica vanadic acid as a heterogeneous, selective and highly reusable catalyst for oxidation of Sulfides at room temperature

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