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Catalytic oxidation of thioanisole Ph–S–CH_3 over VO_x/SiO_2 and VO_x/Al_2O_3 catalysts prepared by sol–gel method

N. Moussa[a,*], José M. Fraile[b], A. Ghorbel[a], José A. Mayoral[b]

[a] *Laboratoire de Catalyse et de Chimie des Matériaux, Département de Chimie, Faculté des Sciences de Tunis,*
Campus Universitaire 2092, ElManar, Tunis, Tunisie
[b] *Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias,*
Universidad de Zaragoza, CSIC, E-50009 Zaragoza, Spain

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Abstract

The catalytic oxidation of thioanisole to the sulfoxide and sulfone using TBHP or H_2O_2 as oxidants in CH_2Cl_2 or MeOH as solvents was carried out over VO_x/SiO_2 or VO_x/Al_2O_3 catalysts prepared by a sol–gel method. It was found that the catalytic activity and selectivity of the reaction depended on the nature of the support (SiO_2 or Al_2O_3), the drying mode (xerogel or aerogel), the calcination of the solid and the vanadium-peroxide species formed. The TBHP/CH_2Cl_2 system gave a very high activity and selectivity, mainly in the cases of vanadia-silica xerogels, with total thioanisole conversion and a sulfoxide/sulfone ratio of 97/3. This activity was truly heterogeneous but vanadium leaching was observed with vanadia-silica aerogels. In contrast, vanadia-alumina catalysts were less active and less selective. The use of the H_2O_2/MeOH system led to vanadium leaching with all types of catalysts.

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1. Introduction

The oxidation of sulfides to sulfoxides and sulfones has been a widely researched subject due to interest in sulfoxides as intermediates in organic synthesis and their presence in biologically active compounds [1]. Sulfoxides are obtained by partial oxidation of sulfides in the presence of an oxidant such as TBHP or H_2O_2 and further oxidation of the sulfoxide leads to the sulfone (Fig. 1)—the extent of this overoxidation reaction depends on the electrophilicity of the oxidant [2].

H_2O_2 and TBHP are relatively weak oxidants and require activation by the addition of transition metal ions to give reactive peroxo species. One example is vanadium (Fig. 2). The reactivity and selectivity depend on the nature of the peroxometal species and its oxidizing power [2–6].

Catalytic epoxidation and sulfoxidation reactions can be carried out in the liquid phase with soluble metal complexes of Ti, V, Re, Mn, Cr, and W [2,7,8]. Easier and more environmentally benign processes can be obtained by replacing homogeneous catalysts with heterogeneous ones [9].

Among the supported metals used in sulfoxidation reactions, titanium is probably most widely employed [9–15]. More recently, reports have been published concerning the preparation of different heterogeneous vanadium catalysts based on titanium oxide [16], mesoporous silica [17], and USY zeolite [18]. Kantam et al. [16] tested $VO(acac)_2$-TiO_2, prepared by impregnation, in the sulfoxidation of thioanisole Ph–S–CH_3; the results showed a thioanisole conversion of 99% in 1.5 h and a sulfoxide/sulfone ratio of 97/3. However, Trukhan et al. [17] found a problem of vanadium leaching into the solution and this accounts for the high thioanisole conversion of 98% after only 4 min. The same leaching problem was also observed in the case of silica-supported titanium catalysts in the same reaction [10]. Leaching resulting from metal-oxygen bond solvolysis is due to the chelating effect of the oxidant and/or the products and by-products, as shown in the epoxidation of allyl alcohol with TS-1 catalyst [19–21].

Most heterogeneous vanadium catalysts are supported catalysts prepared by impregnation. Recently, the sol–gel method has been used for the preparation of vanadia-silica catalysts,

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* Corresponding author.
E-mail address: mnoomen@yahoo.fr (N. Moussa).

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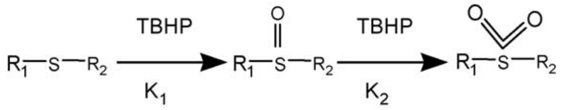

Fig. 1. Oxidation of sulfide.

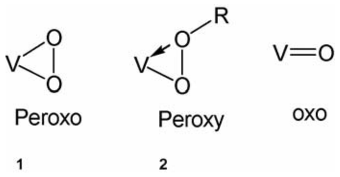

Fig. 2. Different oxidized vanadium species.

which have been tested in reactions such as selective catalytic reduction of nitric oxide with ammonia [22], the oxidation of alkenes [23] and the epoxidation of allyl alcohol [24]. However, the preparation of vanadia-alumina catalysts has not been as widely explored [25]. Supported vanadia catalys have been studied by many spectroscopic techniques in order to establish the effect of the support on vanadia dispersion and the type of vanadium species present [26–35]. Wachs et al. [31,36] and Weckhuysen and Keller [26] recently described the possible structures of supported vanadium species and their effects on the catalytic activity. Different species may be present on SiO_2 and Al_2O_3 supports: isolated VO_4 species, polymeric VO_4 species, crystalline V_2O_5 and mixed oxide with support [26].

In this paper we present the results of our research concerning the catalytic properties of VO_x/SiO_2 and VO_x/Al_2O_3 catalysts, prepared by sol–gel processes, in the oxidation of thioanisole. The work is focused on the effect of the support and the drying mode (xerogel or aerogel) on the reaction selectivity and vanadium stability towards leaching.

2. Experimental

2.1. Preparation of VO_x/SiO_2 and VO_x/Al_2O_3 catalysts

Vanadia-silica gels were prepared by adding $V(acac)_3$ (Fluka, 95%) to a mixture of 1-propanol (Across, 99%) and aqueous HNO_3 (0.7 N). The mixture was stirred at 70 °C until $V(acac)_3$ was completely dissolved, then TEOS (Acros, 98%) in 1-propanol was added to the solution. The total volume of 1-propanol was 16.6 ml. In all preparations the molar composition TEOS:H_2O:HNO_3 was kept constant at 1:4:0.35.

Vanadia-alumina gels were prepared by adding $V(acac)_3$ to a 1M solution of $Al(O\text{-}sBu)_3$ (Acros, 97%) in 2-butanol (Across, 99%). The mixture was stirred at 50 °C for 1 h, until $V(acac)_3$ was completely dissolved. The mixture was cooled to 30 °C and distilled water was added to the solution to give a ratio $H_2O{:}Al = 3$.

In the preparation of both catalysts the V/M (Si, Al) molar ratios were maintained at 0.05, 0.1 and 0.2. The resulting gels were dried either in an oven at 120 °C for 24 h (xerogel), or under supercritical solvent conditions in an autoclave (aerogel). Finally, the solids were calcined under an air flow at 500 °C for 5 h.

2.2. Characterization

The specific surface areas (S_{BET}) and the average pore diameters were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP-2000 instrument. The Raman spectra were recorded on a Renishaw NIR 780TFSeries Laser and the samples were excited with a 785 nm NIR laser, under ambient temperature.

2.3. Sulfoxidation reaction

The oxidant (1.1 mmol), anhydrous TBHP in isooctane (3 M) or H_2O_2 (30% aq), was added to a mixture of thioanisole (1 mmol, Aldrich 99%) and catalyst (25 mg) in the reaction solvent (5 ml), anhydrous dichloromethane or methanol, at 25 °C under argon. The progress of the reaction was followed by GC. Vanadium leaching [19] was assessed by stirring a reaction mixture containing the catalyst for 10–15 min and then removing the catalyst by filtration. The reaction in the resulting solution was monitored by GC.

3. Results and discussion

3.1. Catalyst properties

The specific surfaces areas, average pore diameters and the vanadium loading of the prepared catalysts are presented in Table 1. For the same vanadium loading, VO_x/SiO_2 catalysts develop, in general, higher surface areas than VO_x/Al_2O_3 catalysts. However, the latter have larger average pore diameters, which is of interest because of the easy diffusion of reactants to the active sites.

The Raman spectra of VO_x/SiO_2 xerogels are shown in Fig. 3. At a vanadium loading of 9.74%, two types of vanadium species are detected in the calcined sample; (a) monomeric vanadyl groups (V=O) as revealed by a band near 1025 cm^{-1}, in agree-

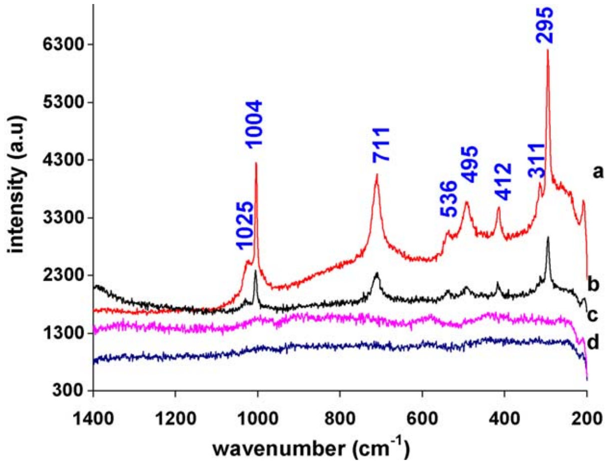

Fig. 3. Raman spectra of VO_x/SiO_2 xerogels: (a) calcined V/Si = 0.2, (b) calcined V/Si = 0.1, (c) non calcined V/Si = 0.2, (d) non-calcined V/Si = 0.1.

Table 1
Textural properties of VO_x/SiO_2 and VO_x/Al_2O_3 catalysts as function of V loading

Drying mode	V/M(Si, Al) nominal ratio	V/Si			V/Al		
		V-content[a] (wt.%)	S_{BET} (m^2/g)	dp[b] (Å)	V-content (wt.%)	S_{BET} (m^2/g)	dp (Å)
Xerogels	0.05	3.35	303	27	2.5	382	118
	0.05C[c]	3.7	225	17	3.2	142	210
	0.1	5.7	306	27	3.7	411	34
	0.1C	6	375	32	5.2	367	32
	0.2	8.2	251	24	6.7	Np[a]	–
	0.2C	11.2	420	23	11.3	Np	–
Aerogels	0.05	2.8	861	46	2.5	414	116
	0.05C	3.7	864	45	2.5	339	114
	0.1	6.6	244	89	5.5	241	192
	0.1C	7.1	264	93	6.1	256	165
	0.2	8.8	526	44	10.9	353	124
	0.2C	9.7	679	47	11.2	378	127

[a] Determined with ICP.

[b] Mean pore diameter determined with BJH method.

[c] C: Calcined. Np: nonporous.

ment with analogous bands found in the case of vanadium catalysts supported on different oxides (silica, alumina, and titania) (1026–1042 cm^{-1}) [33,37–42] or mesoporous vanadium silicates (1030 cm^{-1}) [43], and (b) crystalline V_2O_5 species characterized by peaks at 295, 311, 412, 495, 536, 711, and 1004 cm^{-1}, in agreement with the bands found in the case of vanadium catalysts supported on different oxides (283–285, 305, 405–407, 483–486, 525–527, 699–703 and 995–997 cm^{-1}) [33,37,39]. The same species are detected in the case of the calcined aerogel (Fig. 4a) but in this case with a shift of 10 cm^{-1} towards lower wavenumbers, which indicates that the V=O bond strength is weaker in aerogels than in xerogels [33]. This shift could also be caused by a change in the vanadium coordination or by a decrease in the bond angle or in the bond strength of the –O–V–O– groups bridging V–O–V or V–O–support bonds [44].

Defined peaks were not detected for most of the non-calcined aerogels, a finding that can be attributed to a number of different factors: the high dispersion of vanadium, the poor crystallinity of V_2O_5 or fluorescence phenomena [28].

The Raman spectra of VO_x/Al_2O_3 catalysts are represented in Figs. 5 and 6 for xerogels and aerogels, respectively. In the case of aerogels, significant peaks are not observed and this could be due to fluorescence phenomena [28]. At a vanadium loading of 10.9%, non-calcined xerogels present a Raman band at 1038 cm^{-1}, which is attributed to monomeric vanadyl groups (V=O), and bands towards 964, 698, 573, 472 and 428 cm^{-1}, which can be attributed to polymeric species–probably $(VO_3)_n$ [26,33]. After calcination at 500 °C, VO_x/Al_2O_3 xerogels exhibit a broad band centered at 933 cm^{-1} for vanadium loading of 6.1% and at 967 cm^{-1} for a vanadium loading of 11.2%. These bands correspond to polymeric vanadates [26,33]. None of these frequencies can be assigned to crystalline V_2O_5. An increase in the vanadium loading causes a shift of 10 cm^{-1} towards higher frequency for non-calcined xerogels and a shift of 34 cm^{-1} for calcined ones. This can be attributed to an increase in the chain length of polyvanadate species [33] and, as a consequence,

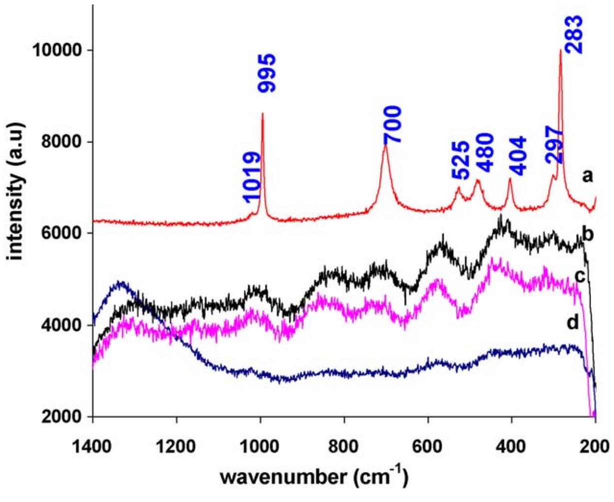

Fig. 4. Raman spectra of VO_x/SiO_2 aerogels: (a) calcined V/Si = 0.2, (b) calcined V/Si = 0.1, (c) non-calcined V/Si = 0.2, (d) non-calcined V/Si = 0.1.

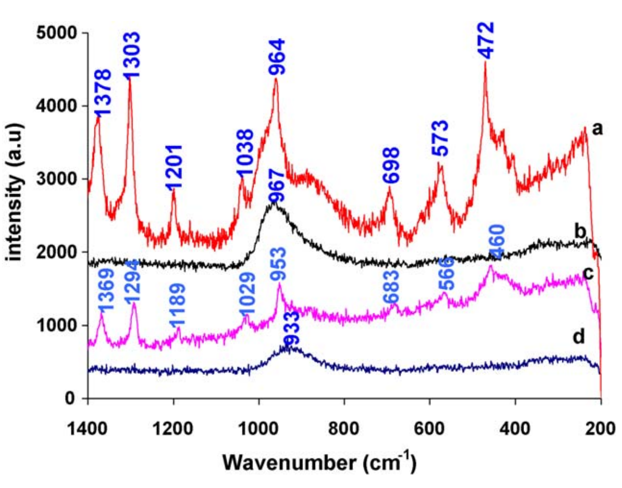

Fig. 5. Raman spectra of VO_x/Al_2O_3 xerogels: (a) non calcined V/Al = 0.2, (b) calcined V/Al = 0.2, (c) non-calcined V/Al = 0.1, (d) calcined V/Al = 0.1.

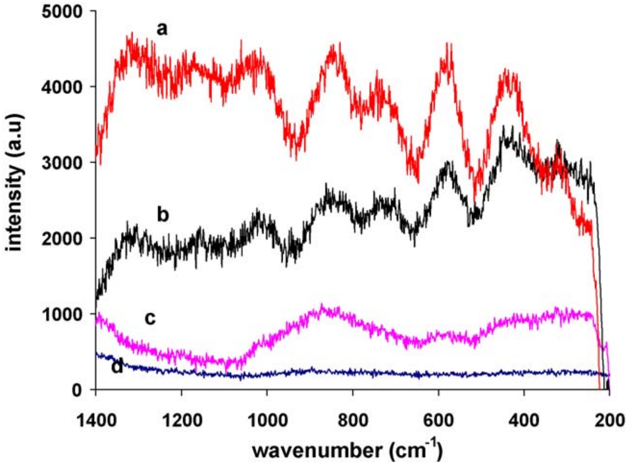

Fig. 6. Raman spectra of VO_x/Al_2O_3 aerogels: (a) non-calcined V/Al = 0.2, (b) non-calcined V/Al = 0.1, (c) calcined V/Al = 0.2, (d) calcined V/Al = 0.1.

an increase in the surface concentration of bridging V—O—V bonds.

Raman spectroscopy shows that the characteristics of the supported vanadium species depend on the nature of the support, the drying method and the calcination. These species are isolated vanadyl species (V=O) and either crystalline V_2O_5 for the SiO_2 support or polyvanadate $(VO_3)_n$ for Al_2O_3.

3.2. Homogeneous reactions

As a control, the homogeneous oxidation of thioanisole with H_2O_2 and TBHP is evaluated. The results presented in Table 2 show that in the absence of catalyst (entries 1, 2) neither H_2O_2 nor TBHP is a powerful oxidant and they have a different effect on the selectivity; TBHP in CH_2Cl_2 is more selective than H_2O_2 in MeOH. The activation of H_2O_2 and TBHP by vanadium precursors such as $V(acac)_3$ and $VO(acac)_2$ accelerates the reaction by forming oxidized vanadium complexes (entries 3–6). The reactivity and selectivity depend on the nature of the vanadium species [5]. Vanadium salts such as $VO(acac)_2$, $V(acac)_3$, $NaVO_3$ and V_2O_5 form peroxocomplex **1** or peroxycomplex **2** in the presence of H_2O_2 and TBHP, respectively [5].

When the $V(acac)_3$/TBHP complex is used, a sulfoxide/sulfone ratio of 92/8 is obtained and this is better than that observed with the $VO(acac)_2$/TBHP complex (sulfoxide/sulfone ratio = 86/14). Furthermore, the use of H_2O_2 leads to no difference between $V(acac)_3$ and $VO(acac)_2$ and a fast thioanisole conversion and lower selectivity are obtained. These findings reflect the stronger oxidizing power of peroxovanadium species **1** formed with H_2O_2 in comparison to the peroxyvanadium species **2** obtained with TBHP. These results confirm that sulfur oxidation with TBHP is more selective than that with H_2O_2, as in the case of the epoxidation reaction [5].

From this study, it is clear that both activity and selectivity depend on the species formed between vanadium and the oxidant (TBHP or H_2O_2).

3.3. Heterogeneous reactions with TBHP

The results of the TBHP oxidation of thioanisole with VO_x/SiO_2 catalysts are gathered in Table 3.

Xerogels (entries 1–6) exhibit a high sulfide conversion with high sulfoxide selectivity. Almost total conversion can be obtained after 6 h with a sulfoxide/sulfone ratio of 96/4. Only marginal differences are observed between the calcined and non-calcined xerogels. In general, the calcined xerogels are slightly less selective and more active, especially the solid with a high vanadium loading.

In all cases the heterogeneous nature of the reaction is tested by filtration under reaction conditions at short reaction time and monitoring the solution. Except for xerogel with V/Si = 0.05, oxidation activity is not observed in the solutions with other VO_x/SiO_2 xerogels, indicating that leaching of active vanadium to the solution does not occur.

In contrast, VO_x/SiO_2 aerogels exhibit a very high activity, with a thioanisole conversion above 95% in only 1–2 h. The filtration experiments show that this activity is due in part to soluble vanadium leached from the solids. Vanadium leaching was also observed by Trukhan et al. [17] and Fuerte et al. [18]. The reactions are performed under the same conditions for both xerogels and aerogels and vanadium leaching can therefore be explained in terms of weaker bridging O–V–O– groups [37], as shown by

Table 2
Homogeneous liquid phase oxidation of thioanisole

Entry	Catalyst	Oxidant	Solvent	Time	Thioanisole conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)
1	—	TBHP	CH_2Cl_2	24 h	30	98	2
2	—	H_2O_2	MeOH	30 h	22.5	71	29
3	$V(acac)_3$	TBHP	CH_2Cl_2	1 min	25	94	6
				25 min	92	96	4
				1.5 h	96	92	8
4	$VO(acac)_2$	TBHP	CH_2Cl_2	1 min	78	93	7
				25 min	98	88	12
				1.5 h	98	86	14
5	$V(acac)_3$	H_2O_2	MeOH	1 min	92	85	15
6	$VO(acac)_2$	H_2O_2	MeOH	1 min	92	85	15

Entries 1, 2: reaction was carried out without catalysts. Thioanisole: oxidant: vanadium = 1:1.1:0.1 (molar ratio), solvent = 5 ml, $T = 25\,^{\circ}C$.

Table 3
Thioanisole oxidation with TBHP over VO_x/SiO_2 catalysts

Entry	Drying mode	V/Si nominal ratio	Thioanisol conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)	Time (h)	Observation[a]
1	Xerogel	0.05	95	96	4	3	Homogeneous
2		0.05C[b]	92	97	3	3	Homogeneous
3		0.1	99	94	6	6	Heterogeneous
4		0.1C	99	91	9	6	Heterogeneous
5		0.2	83	97	3	8	Heterogeneous
6		0.2C	99	94	6	6	Heterogeneous
7	Aerogel	0.05	99	91	9	1	Homogeneous
8		0.05C	99	82	18	1	Homogeneous
9		0.1	95	97	3	1.5	Homogeneous
10		0.1C	95	97	3	1	Homogeneous
11		0.2	99	91	9	1	Homogeneous
12		0.2C	97	90	10	1	Homogeneous

Thioanisole: oxidant = 1:1.1 (molar ratio), solvent = 5 ml, $T = 25\,°C$.

[a] Heterogeneous: without vanadium leaching. Homogeneous: with vanadium leaching.

[b] C: calcined.

the Raman spectra. These results demonstrate that vanadium stability in heterogeneous catalysts prepared by a sol–gel process depends on the drying mode.

The results of thioanisole oxidation over VO_x/Al_2O_3 catalysts are given in Table 4. In the case of xerogels, thioanisole conversion and sulfoxide selectivity increase with increasing V/Al ratio and calcination is crucial in obtaining active catalysts, mainly at low vanadium loadings. Among the calcined xerogels, the best conversion (62% in 9 h) and selectivity (sulfoxide/sulfone ratio = 97/3) were obtained with the catalyst with the highest vanadium loading, although this catalyst is nonporous (see Table 1).

The effect of calcination is not so positive with aerogels. An increase in thioanisole conversion is only observed at a high vanadium loading: With calcined aerogels thioanisole oxidation to sulfoxide is the primary reaction, but after 1 h the sulfoxide concentration is sufficiently high to lead to sulfone formation. The evolution of the conversion and the selectivity in the thioanisole oxidation with TBHP over calcined and non-calcined aerogels for a vanadium loading of 2.46% are shown in Figs. 7 and 8. The sulfoxide selectivity, although always low, is slightly better with non-calcined aerogels. On the other hand, the results show that aerogels exhibit a higher activity but a lower selectivity than xerogels.

The results in Tables 3 and 4 illustrate that VO_x/SiO_2 catalysts are more active and selective than VO_x/Al_2O_3 catalysts. The differences in activity and selectivity between VO_x/SiO_2 and VO_x/Al_2O_3 confirm the existence of different vanadium species, which are further highlighted by the Raman spectroscopy. From a correlation of the activity and spectroscopic results, it seems that the V_2O_5 present on silica-supported catalysts is more selective than the polyvanadate groups detected on alumina. Furthermore, the low reactivity of VO_x/Al_2O_3 may be related to the presence of relatively unreactive polymerized surface vanadia species.

A change in the support provides indirect evidence for the role of the bridging V–O–support bonds in determining the catalyst activity and the homogeneity or heterogeneity of the sulfoxi-

Table 4
Thioanisole oxidation with TBHP over VO_x/Al_2O_3 catalysts

Entry	Drying mode	V/Al nominal ratio	Thioanisol conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)	Time (h)	Observation[a]
1	Xerogel	0.05	0	–	–	3	Inactive
2		0.05C[b]	13	79	21	8	Heterogeneous
3		0.1	0	–	–	6	Inactive
4		0.1C	51	78	22	6	Heterogeneous
5		0.2	33	97	3	6	Heterogeneous
6		0.2C	39	97	3	6	Heterogeneous
7	Aerogel	0.05	52	79	21	7	Heterogeneous
8		0.05C	43	68	32	7	Heterogeneous
9		0.1	62	72	27	7	Heterogeneous
10		0.1C	65	55	45	6	Heterogeneous
11		0.2	51	71	29	2	Partially homog.
12		0.2C	77	67	33	2	Partially homog.

Thioanisole: oxidant = 1:1.1 (molar ratio), solvent = 5 ml, $T = 25\,°C$.

[a] Heterogeneous: without vanadium leaching. Homogeneous: with vanadium leaching.

[b] C: calcined.

Table 5
Thioanisole oxidation with H_2O_2 over typical VO_x/SiO_2 and VO_x/Al_2O_3 catalysts

V/M ratio	Catalyst	Thioanisole conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)	Time	Observation
V/Si = 0.2	Calcined xerogel	90	ND	ND	10 min	Homogeneous
	Calcined aerogel	98	81	19	1 min	Homogeneous
V/Al = 0.2	Calcined xerogel	35	55	45	24 h	ND
	Calcined aerogel	94	83	17	30 min	Partially homogeneous
	Recovered calcined aerogel	14	56	44	25 min	ND

ND: not determined. Thioanisole: oxidant = 1:1.1 (molar ratio), solvent = 5 ml, $T = 25\,°C$.

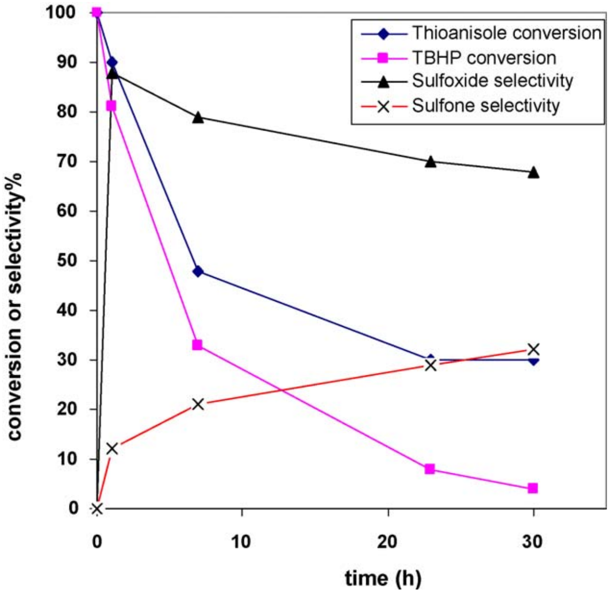

Fig. 7. Kinetic of sulfoxidation of thioanisole over non calcined V/Al = 0.05 aerogel catalyst.

dation reaction. Since vanadium bonds to alumina are known to be stronger than in silica [26,34], an extremely strong bond with the surface seems to be detrimental to the activity and selectivity. However, an extremely weak bond, as in the case of VO_x/SiO_2 aerogels, leads to significant leaching of active vanadium species. The best compromise between catalytic performance (better with weaker bonds) and stability (better with stronger bonds) seems to be the VO_x/SiO_2 xerogel system, whose medium strength V–O–Si bonds give rise to a stable solid with high catalytic activity and excellent sulfoxide selectivity.

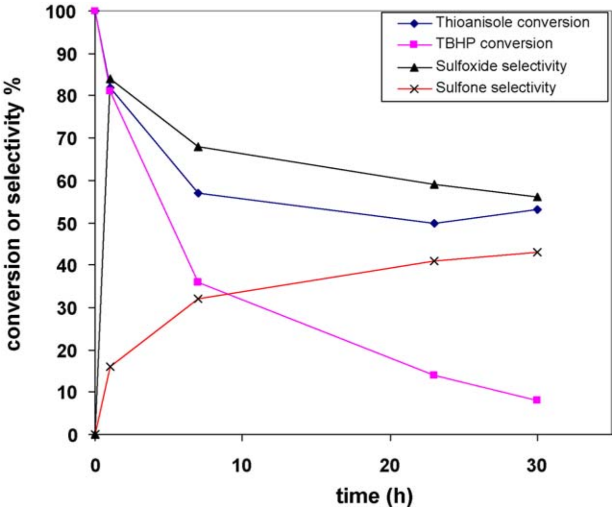

Fig. 8. Kinetic of sulfoxidation of thioanisole over calcined V/Al = 0.05 aerogel catalyst.

3.4. Heterogeneous reactions with H_2O_2

Finally, it is of interest to assess the stability of vanadium in the H_2O_2/MeOH medium. This study was carried out on the calcined catalysts with the highest vanadium loading.

The results presented in Table 5 show that the use of calcined silica-based catalysts gives a thioanisole conversion higher than 90% in just a few minutes. The test for leaching showed that this activity is due to the presence of homogeneous catalyst from vanadium leaching. The ready solubility of vanadium in the presence of H_2O_2 (compared to TBHP) is probably due to the formation of the peroxovanadium complex **1**, which is more stable than peroxyvanadium complex **2** [6].

The calcined alumina xerogel leads to a lower conversion with H_2O_2 than with TBHP. The selectivity is also significantly reduced and is even lower than that obtained in the non-catalyzed homogeneous reaction. The calcined alumina aerogel shows a better activity, but again this is due in part to leaching of active vanadium species. The recovery of the aerogel for reuse gave rise to a reduction in activity and also in selectivity. This selectivity is identical to that obtained with the calcined xerogel, which seems to indicate that oxidation on both solids takes place through the same intermediate, probably due to a similarity between the two surface vanadium species.

4. Conclusion

VO_x/SiO_2 and VO_x/Al_2O_3 catalysts with different V/M (Si, Al) ratios were prepared by a sol–gel method. The effect of the support, the drying mode (xerogel or aerogel), the V/M ratio and calcination were studied in the oxidation of thioanisole. Catalytic tests showed that VO_x/SiO_2 xerogels are the most active and selective systems, with a thioanisole conversion of 98% and a sulfoxide/sulfone ratio of 97/3. On the other hand, VO_x/SiO_2 aerogels are very active but less selective than xerogels, although this high activity is due to vanadium leaching in the solution.

The stability of vanadium on the catalysts depends on the vanadium-support interaction, which is weaker in aerogels than in xerogels. In the range of V/Si ratios selected we did not notice any effect of calcination on the thioanisole oxidation and only the drying mode has a critical effect on the vanadium stability.

VO_x/Al_2O_3 catalysts are less active and less selective than VO_x/SiO_2 catalysts. This difference in activity and selectivity with the change in support indicates the role of the bridging V–O–support bonds. Raman spectroscopy shows the existence of crystalline V_2O_5 on the silica support and polyvanadates on the alumina support–these findings explain the differences in activity and selectivity. The low activity of VO_x/Al_2O_3 could be related to the presence of relatively unreative polymerized surface vanadia species.

Complexation of vanadium species by different oxidants, such as H_2O_2 or TBHP, involves the formation of diverse peroxovanadium species that give rise to distinct activity and selectivity. This observation indicates that activity and selectivity are related, not only to the vanadium species but also to the peroxovanadium species. The use of different oxidants indicates that vanadium is not stable toward leaching, particularly with H_2O_2.

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