

Vanadium sites in V-K10: Characterization and catalytic properties in liquid-phase sulfide oxidation

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Abstract

Vanadium-containing K10 was synthesized and characterized by electron paramagnetic resonance, nuclear magnetic resonance, N₂ adsorption at 77 K and chemical analysis. Two different vanadium species have been identified in dried V-K10, the first is V⁴⁺ in square pyramidal or distorted octahedral environment and the second is V⁵⁺ in a tetrahedral environment that is present in an isolated monomeric state (VO₄³⁻) and dimeric state [O₃V–O–VO₃]⁴⁻. When V-K10 was calcined in air, V⁴⁺ was oxidized to V⁵⁺ with a change in the coordination from square pyramidal or distorted octahedral to tetrahedral. Vanadium species, in the highest oxidation state (V), were found to be the catalytic sites that readily interact with *tert*-butylhydroperoxide (TBHP) to offer an active and selective catalytic system for the oxidation of sulfides. This catalytic system was studied in the asymmetric oxidation of methyl phenyl sulfide, using two types of chiral modifier, and gives excellent conversions and sulfoxide selectivity, together with an enantioselectivity in the range of 9–11% ee.

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1. Introduction

Clays have been widely used as catalysts and supports in a large variety of organic reactions [1,2]. Clay-based catalysts are often obtained by modifications with transition metals through either cationic exchange or pillaring [3,4].

Vanadium is a key component of many solids which have been found to exhibit excellent catalytic properties in redox reactions that encompass the oxidation of a variety of organic substrates [5]. In spite of this, the use of vanadium-modified clays as oxidation catalysts has been rather scarce [6–10] and has mainly focused on the incorporation of vanadium into Al-, Ti-, or Zr-pillared clays. We have shown [11] that the use of natural montmorillonite as a support for the vanadium phase leads to solids with a poor porous structure and a low surface area.

Acid treatment is another system to activate clays for use as catalyst or supports [12]. One commercial example is K10 montmorillonite, which is obtained from the natural montmorillonite

by treatment with mineral acids at high temperature. The natural montmorillonite structure is progressively destroyed, which results in a loss of crystallinity but a significant increase in surface area and acidity in comparison to the natural clay [13]. These features of K10 montmorillonite have proved to be positive in the preparation of vanadium catalysts [14].

In the present work we describe how the use of K10 allows the preparation of a vanadium supported K10 catalyst (V-K10) containing accessible and isolated vanadium sites, as shown by different spectroscopic techniques. These sites are able to catalyze the selective oxidation of sulfides to sulfoxides, with high yield and selectivity, using *tert*-butylhydroperoxide (TBHP) as the oxidant.

2. Experimental

H-K10, was prepared from K10 by treatment with 0.1 N HCl solution [14]. Vanadium catalyst was obtained by heating VCl₃ (5 mmol) under reflux in dry *t*-BuOH (20 ml) with H-K10 (1 g) under a helium atmosphere until the solid clay suspension turned to a deep green in colour (within approximately 6 h). The

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solid was filtered and washed several times with dry *t*-BuOH to remove the excess of VCl_3 , then oven dried at 383 K, and calcined in dry air at different temperatures.

K10 and V-K10 calcined at different temperatures were characterized by several techniques. Chemical analysis was carried out by atomic absorption spectrometry on a Perkin-Elmer 3100 apparatus after sample dissolution through acid attack. BET surface areas and pore volumes of the samples were measured on a Micrometrics ASAP 2000 apparatus. ESR spectra were recorded with a Bruker ER 200tt spectrometer at 77 K and room temperature. A Bruker MSL 400 spectrometer was used to obtain ^{51}V -MAS-NMR spectra. The catalytic properties of V-K10 were tested in oxidation of sulfide (7 mmol) to sulfoxide, which was performed by stirring 30 mg of V-K10 in the presence of *tert*-butylhydroperoxide (7 mmol) in dry dichloromethane (DCM) under an inert atmosphere, followed by the addition of the sulfide. The reaction was monitored by gas chromatography (SPBTM-5 Capillary Column, 30 m \times 0.25 mm \times 0.25 μm).

3. Results and discussion

3.1. Textural and chemical analyses

The results obtained from chemical and textural analyses of the different samples are shown in Table 1. As it can be seen, the introduction of vanadium leads to a decrease of surface area and pore volume, a change that can be attributed to the filling of pores with vanadium species. N_2 adsorption isotherms of K10 and VK10 show that their large surface areas are mainly due to mesopores, with a negligible microporosity, and a pore size distribution and an average pore diameter of 54–65 nm. Changes in chemical analysis and surface area results observed upon calcination suggest changes in the structure of the vanadium sites, a situation in agreement with the spectroscopic studies described below.

3.2. ESR spectroscopy

In order to gain insight into the location and the nature of the vanadium centres, ESR investigations have been undertaken. The samples show a signal (Fig. 1) typical of $\text{V(IV)} 3d^1$ centres, with eight-line hyperfine patterns derived from the interaction of the free unpaired electron of V^{4+} and the nuclear magnetic moment of ^{51}V ($I = 7/2$). The spectrum is very similar to those obtained by Rigutto and al. [15] at 77 K, showing a monomeric vanadyl-like species, with g and A anisotropic tensor values (as

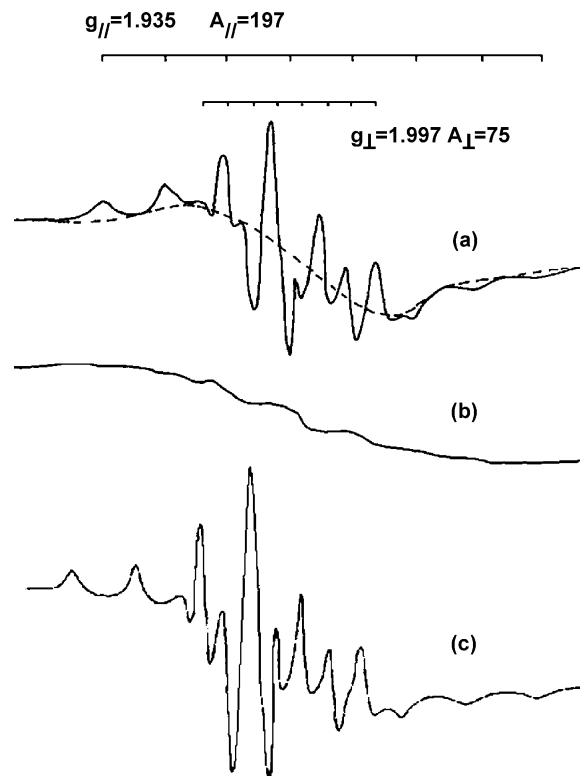


Fig. 1. ESR spectra of V-K10 dried at 383 K (a), calcined at 573 K (b) and after alcohol adsorption on calcined sample at 573 K (c).

deduced from the signal) that are characteristic of both square pyramidal or distorted octahedral coordination with approximate axial symmetry.

The spectra exhibit a well-resolved hyperfine structure, indicating good dispersion of vanadium, but the baseline is not horizontal. A superimposed broad singlet (marked with a dashed line), is observed and can be attributed to V^{4+} in dipolar interaction with other V^{4+} ions. Similar spectra were obtained by Taouk [16]. It has been shown that the close proximity of a high number of paramagnetic centres results in an electronic exchange between several of them and, as a consequence, only one line is observed. It can be concluded that, the broadening of the signal indicates an increase in the integral of exchange and the dipolar interaction between paramagnetic centers [17].

The spectra of V^{4+} in tetrahedral coordination show different parameters: V^{4+} in ThGeO_4 shows [15] $g_{\parallel} = 1.831$, $g_{\perp} = 1.980$ and $A_{\parallel} = 191\text{ G}$, $A_{\perp} = 35\text{ G}$; in $\text{Ga}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ [18] $g_{\parallel} = 1.855$, $g_{\perp} = 1.98$ and $A_{\parallel} = 152\text{ G}$, $A_{\perp} = 30\text{ G}$. Moreover, those spectra are detected only at 77 K or at lower temperature [19], whereas our spectra recorded at 77 K and room temperature are identical, with a lower intensity of the signal at room temperature. These results enable the tetrahedral symmetry of the V^{4+} environment to be ruled out.

The signal intensity decreases with increasing calcination temperature in air (Fig. 1b). This observation can be explained by a change in the oxidation state from V^{4+} to V^{5+} (d^0). Reduction of vanadium (V) in calcined samples to the (IV) state was performed by adsorption of organic molecules such as ethanol (Fig. 1c). The ESR spectrum recorded for the sample

Table 1
Results of chemical analysis and textural properties of the samples

Sample ^a	V content (% weight)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)
H-K10	–	233	0.31
V-K10 (383)	1.72	133	0.22
V-K10 (473)	1.72	162	0.25
V-K10 (573)	1.92	155	0.25

^a In parentheses the temperature of treatment.

obtained in this way is identical to the spectrum of the dried sample (Fig. 1a). These results indicate that V-K10 exhibits redox properties and readily changes oxidation state between V^{4+} and V^{5+} .

3.3. Solid state NMR spectroscopy

^{51}V -MAS-NMR studies on V-containing catalysts have shown that it is possible to obtain information on the symmetry environment of vanadium by comparison with model compounds. The spectra obtained for dried and calcined V-K10 samples are gathered in Fig. 2. In the case of the dried sample (Fig. 2a), two broad peaks at -616 and -722 ppm can be seen. Peaks centered near -600 ppm have been also found in the case of vanadium-sepiolite [20], vanadophosphate glasses [21], and vanadium mesoporous materials [22]. According to Ocelli et al. [20] this signal can be assigned to four-coordinate vanadium (V), similar to site 1 in $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ that appears at -610 ppm (-620 ppm from other authors [23]). In fact, this similarity seems to indicate the presence of dimeric species, analogous to $[\text{O}_3\text{V}-\text{O}-\text{VO}_3]^{4-}$, in V-K10.

The line at -722 ppm is however more difficult to assign. A signal at -680 ppm detected in vanadophosphate glasses [21], was assigned to octahedral VO_6 units. However, it is generally accepted that octahedral vanadium appears at around -300 ppm, as occurs in V_2O_5 [22,24], and this signal is not detected in V-

K10. In the case of crystalline mesoporous molecular sieves [25] a band with δ_i of -710 ppm is described in dehydrated samples and assigned to a surface $(\text{SiO})_3\text{V}=\text{O}$ species. This band is shifted to -580 ppm upon hydration in a reversible process.

However, this behaviour is not observed in V-K10, as calcination of the sample in air at 573 K (Fig. 2b) leads to a decrease in the intensity of the signal around -722 ppm, while the signal at -616 ppm becomes more prominent. Condensation from monomeric $(\text{SiO})_3\text{V}=\text{O}$ species to dimeric or oligomeric $\text{O}_3\text{V}-\text{O}-\text{VO}_3$ species may account for this behaviour.

All these findings, show that vanadium atoms can be present in dried V-K10 simultaneously in two valence states and at least two different coordination states: V^{4+} square pyramidal or distorted octahedral (indicated by EPR) and monomeric or oligomeric tetrahedral V^{5+} (shown by ^{51}V -MAS-NMR). When V-K10 was calcined in air, V^{4+} was oxidized to V^{5+} and its square pyramidal or distorted octahedral structure transformed into tetrahedral one.

3.4. Tert-butylhydroperoxide interaction with vanadium sites

The study of the epoxidation of allylic alcohol over V-K10 [26] had shown that the oxidant TBHP (*tert*-butylhydroperoxide) is an efficient competitor of allylic alcohol in binding vanadium centers. In an attempt to study the species responsible for the oxidation reactions, the effect of TBHP adsorption onto the calcined V-K10 was followed by ESR and NMR spectroscopy. When V-K10 calcined at 573 K was treated with TBHP and dried under vacuum at room temperature, an ESR spectrum was recorded and characterized by the following spectroscopic factors: $g_1 = 2.032$; $g_2 = 2.010$ and $g_3 = 2.001$ (Fig. 3). The signal may result from the presence of $t\text{BuOO}^\circ$ species [26], stabilized by vanadium (V), which lead to the formation of *tert*-butylhydroperoxide-vanadium intermediate (1).

This intermediate was also studied using ^{51}V -MAS-NMR (Fig. 4). When V-K10, calcined at 573 K, was impregnated at room temperature with a solution of TBHP in dichloromethane, three relatively sharp peaks appeared while the broad signal nearly vanished. It appears that all of the vanadium species react with TBHP. According to Rigutto and Van Bekkum [15], the *tert*-butyl peroxy complexes give signals at -526 and -546 ppm in VAPO, whereas the coordination of *tert*-butanol gives rise to signals at -605 and -680 ppm. Thus, we can assign the signal at -526 ppm to a peroxy compound ($\text{V}-\text{O}-\text{O}-t\text{-Bu}$), the signal at -680 ppm to *tert*-butanol-coordinated center ($\text{V}-\text{O}-t\text{-Bu}$) and the signal at -578 ppm to a combination of those at -546 (peroxy) and -605 (*tert*-butanol-coordination) Fig. 5.

It can be concluded that the *tert*-butylhydroperoxide-vanadium intermediate is first formed and then reacts with alcohol. The decomposition of TBHP over V-K10 was very slow at room temperature, at least in the absence of an oxidizable substrate.

Taking in account these results of TBHP adsorption on the catalyst surface, it may be assumed that the activity of V-K10 in this reaction result from the site isolation of vanadia center, which may be vanadyl species in its highest oxidation state

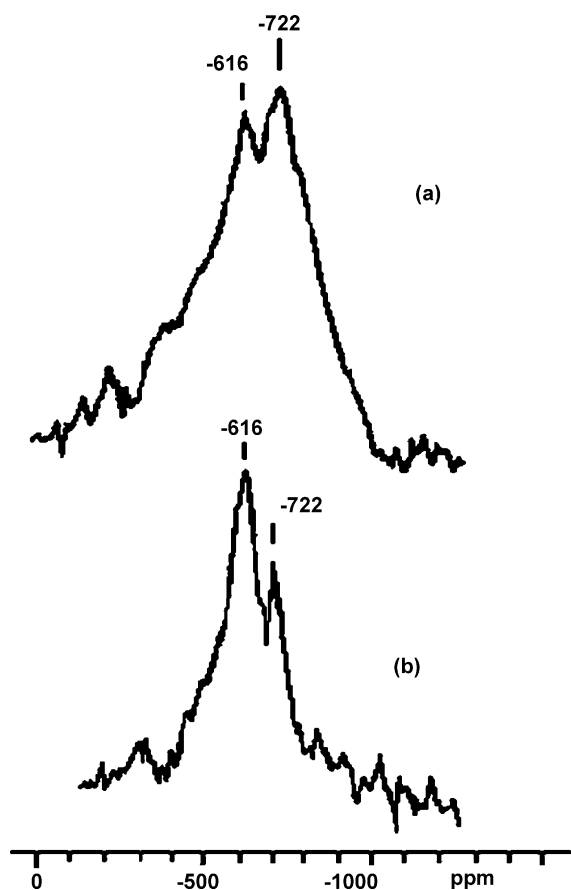


Fig. 2. ^{51}V RMN spectra of V-K10 dried at 383 K (a) and calcined at 573 K (b).

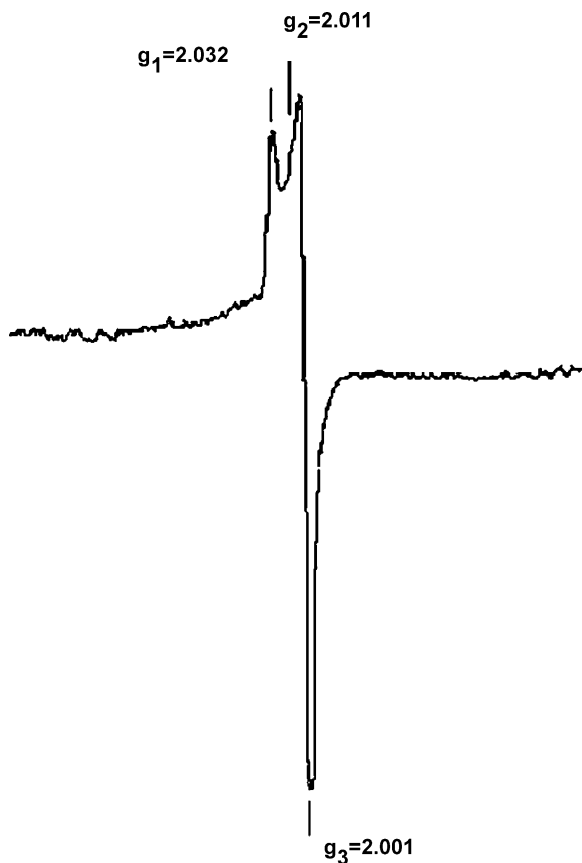


Fig. 3. ESR spectrum of V-K10 calcined at 573 K impregnated with TBHP.

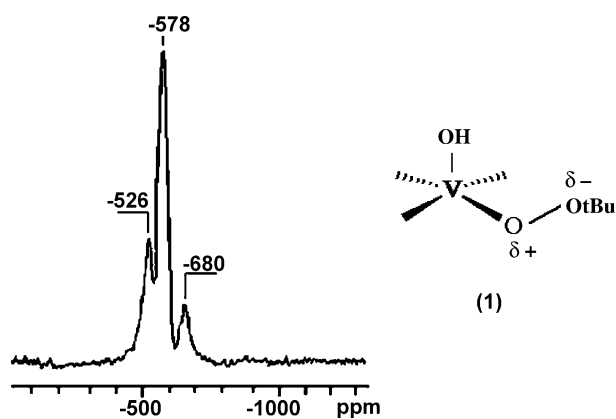
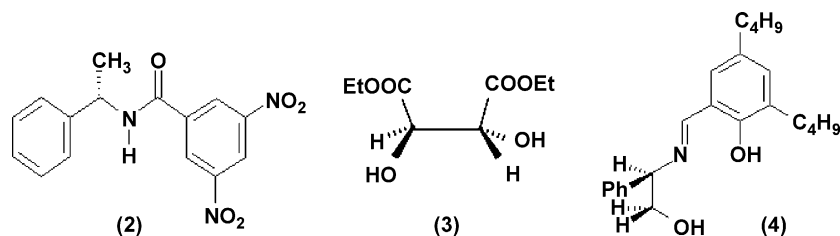
Fig. 4. ⁵¹VNMR spectrum of V-K10 calcined at 573 K impregnated with TBHP.

Fig. 5. Chiral shift reagent (2) and chiral ligands (3, 4).

Table 2
Oxidation of several sulfides catalyzed by V-K10

Substrate	t (h)	Conversion (%)	Sulfoxide (%)	Sulfone (%)
Butylmethylsulfide	9	84	98	2
Thioanisole	9	81	97	3
Tetrahydrothiophene	5	81	97	3
2-Methylthiophene	24	0	–	–

Reaction conditions: catalyst V-K10 calcined at 300 °C, 30 mg; sulfide, 7 mmol; oxidant (TBHP), 7 mmol; DCM at room temperature.

(V=O)³⁺. The vanadium in low oxidation state is rapidly oxidized by *tert*-butylhydroperoxide to its highest oxidation state. The geometry of the intermediate complex **1** makes the peroxidic oxygens more electrophilic and, hence, more liable to nucleophilic attack by the substrates to be oxidized.

3.5. Catalytic oxidation of sulfides on V-K10

The above results prompted us to study V-K10 as an oxidation catalyst and the selective oxidation of sulfides to sulfoxides was selected as the benchmark reaction. The results obtained using different sulfides are given in Table 2. As it can be seen most of the substrates are oxidized to give high yields and excellent sulfoxide selectivities. The high selectivities as the lack of reaction with thiophene are consistent with the mechanistic hypothesis propose on the basis of the spectroscopic studies, i.e., the reagent acts as a nucleophile attacking the TBHP, which is activated by coordination to the vanadium catalytic sites.

3.6. Asymmetric oxidation of methyl phenyl sulfide on V-K10 with a chiral modifier

Chiral vanadium complexes have proved to be useful catalysts in several asymmetric oxidations [27]. This fact, together with the usefulness of the optically active sulfoxides in asymmetric synthesis of organic compounds, prompted us to study the effect of several chiral modifiers on V-K10 catalyst. The results obtained in the asymmetric oxidation of methyl phenyl sulfide are gathered in the Table 3.

It can be seen that the addition of these modifiers markedly the catalytic activity but maintains a high sulfoxide selectivity. Tartrate derivatives have been described as chiral ligands for the same reaction in homogeneous phase [29] and with solid titanium catalysts [30]; in the later case the catalyst is more active but leads to a very similar 10% ee. The second modifier used is a chiral Schiff base (4), which was synthesized by the condensation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with a chiral β-amino alcohol in methanol [31]. The use of this ligand

Table 3
Results obtained in the asymmetric oxidation of methyl phenyl sulphide

Chiral modifier	<i>t</i> (h)	Conversion (%)	Sulfoxide (%)	Sulfone (%)	ee (%)
(+) DET (3)	7	50	95	5	9
Schiff Base (4)	48	25	>99	–	11

Reaction conditions: catalyst V-K10 calcined at 300 °C, 30 mg; sulfide, 7 mmol; oxidant (TBHP), 7 mmol; DCM; temperature, –15 °C; chiral modifier/V = 1:1. The e.e.s were determined from the ¹H-NMR spectrum in the presence of the chiral shift reagent (2).

does not noticeably improve enantioselectivity but the catalytic activity is even lower.

The reduced catalytic activity indicates that the chiral modifier is coordinated to the catalytic centres, a situation in agreement with the low but significant enantioselectivity. These results open the way to further developments in this area.

4. Conclusion

The spectroscopic techniques adopted in this study indicate the presence of vanadium in dried V-K10 in two different states, tetrahedral V⁵⁺ and both square pyramidal or distorted octahedral V⁴⁺. In the case of the sample calcined at 573 K, the vanadium is present mainly in V⁵⁺ state with a tetrahedral coordination as both monomeric and dimeric species and these species can be reversibly transformed between V⁴⁺ and V⁵⁺ states. V-K10 is efficient for the selective sulfide oxidation reaction and this is probably due to the well-dispersed state of the active species (V=O)³⁺_{tet} via the *tert*-butyl hydroperoxide-vanadium intermediate. VK10, when modified by chiral ligands, shows a reduced catalytic activity in the asymmetric oxidation of methyl phenyl sulfide, leading to a low but significant 9–11% of enantiomeric excess (e.e.).

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