SHORT PAPER

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Physicochemical properties of vanadium-containing montmorillonite in epoxidation of allylic alcohol[†]

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Vanadium-containing aluminosilicate molecule sieves were observed to exhibit remarkable catalytic activity in oxidation of hydrocarbons, notably epoxidation of allylic alcohol. In this paper, we review the spectroscopic characterisation of framework incorporation and redox behavior of vanadium in both natural montmorillonite and K10. NMR and EPR studies of coordination and oxidation state of vanadium in dried and calcined samples show that vanadium exists mainly in a tetrahedral oxygen coordination as an isolated monomeric state (VO_4^{3-}) in V-mont and also as dimeric state $[O_3V\text{-}O\text{-}VO_3]^{2-}$ in V-K10 case. The vanadium, in both systems, shows redox properties, changing its oxidation state readily between V^{4+} and V^{5+}. The development of a high surface area in the V-K10 case, provides a well-dispersed vanadium species, which inceases the initial rate compared to the V-mont one. This vanadium species, in highest oxidation state (V), is found to be the catalytic centre in epoxidation of allylic alcohols, according to a heterolytic mechanism via a *tert*-butylhydroperoxide-vanadium intermediate.

Keywords: montmorillanite, epoxidation, allylic alcohal

Vanadium is the key component of many solid catalysts of redox processes such as the oxidation of a variety of organic substrates, notably epoxidation of allylic alcohol.

Nevertheless, few reports have dealt with vanadium containing montmorillonite. On the other hand, a large number of techniques including FTIR, EPR and ^{51}V solid state NMR provided strong evidence that the vanadium is located in the montmorillonite framework probably at a defect site.[1,2]

In the present work, the local environment of the framework vanadium ions in two types of clay with the structure of natural montmorillonite (CECA France) or K10 montmorillonite is investigated by means of solid state ^{51}V-NMR in addition to techniques that have been used previously. Subsequently, the catalytic activity of V-K10 and V-mont in the epoxidation reaction of allylic alcohol with TBHP (tert-butylhydroperoxide) is described and explained in terms of the local environment and oxidation state of vanadium.

Experimental

The K10 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.[3] H-montmorillonite and H-K10, were prepared from natural clay and K10, by treatment with 0.1N HCl solution.[4] V-mont and V-K10 catalysts were obtained by refluxing VCl_3 (5mmol) in dry *t*BuOH (20 ml) with H-montmorillonite or H-K10 (1g) under a helium atmosphere until the solid clay suspension turned to a deep green colour (within approximatively 6 h). The solids were filtered and washed many times with dry tBuOH to remove the excess of VCl_3 and then oven dried at 383K and calcined at different temperatures.

All samples were characterised by BET surface area and porosity measurements. To get further insight about the location and the nature of vanadium species present in these catalysts, ESR, NMR and IR investigations were performed on all samples.

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. Infrared study was realised with Perkin-Elmer FTIR paragon 1000PC. EPR spectra were recorded with a Bruker ER spectrometer 200tt at 77K using 30mg samples. A Bruker MSL 400 spectrometer was used for NMR spectra registration with 20mg samples.

Results and discussion

Study of precursor solution: In the first step of the catalyst preparation, the precursor solution VCl_3 / *t*BuOH was examined by V^{51}NMR and EPR spectroscopy in order to ascertain the coordination sphere of the vanadium species before intercalation into the clay.

Figure 1 shows the occurrence of two peaks in the NMR spectrum, which may be indicative of two vanadium species with different local coordinations. In their ^{51}V NMR study of vanadium species in solution, Howarth *et al.*,[5] assigned the signals at –536 and –676ppm (relative to $VOCl_3$) to vanadium in a tetrahedral coordination of $[VO_3(OBu^t)]^{2-}$ and $VO(OBu^t)_3$ species. This result proves the

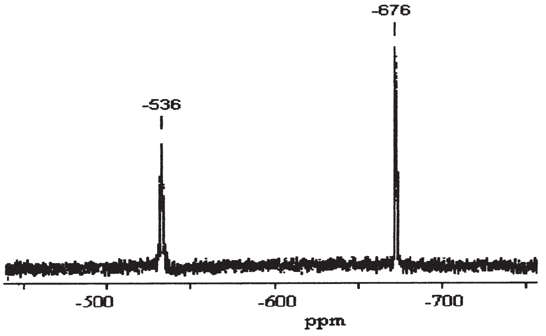

Fig. 1 ^{51}V NMR spectrum of VCl_3 in Bu^tOH.

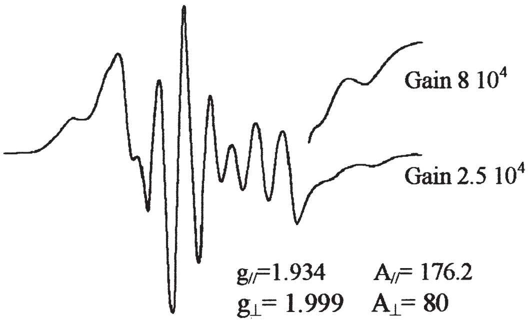

Fig. 2 EPR spectrum of VCl_3 in Bu^tOH.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Results of chemical analysis (vanadium weight-%) and textural properties of the samples

Samples	V%	S_{BET}(m^2/g)	Total pore volume (cm^3/g)
mont^a	——	40.8	0.10
mont^b	——	41.5	0.10
V-mont ^{a}	5.61	36.2	0.14
V-mont ^{b}	6.00	18.0	0.09
K10^a	——	233.8	0.31
K10^b	——	368.1	0.50
V-K10 ^{a}	8.80	133.3	0.22
V-K10 ^{b}	9.80	155.3	0.25

^{a} Dried at 383K and ^{b} calcined at 573K.

presence of vanadium in the state V, but does not eliminate its presence in the state IV. In fact, an EPR study shows a signal with an hyperfine structure, typical of V^{4+} species in vanadyl group VO^{2+} (Fig. 2). It may be concluded that the vanadium centre occurs, in precursor solution, in two valence state V (IV) and V (V).

In both case the treatment with vanadium solution decreases the surface area. This can be attributed to the filling of pore volume with vanadium species. This effect is more pronounced in the V-K10 case, which is due to its higher vanadium content compared to V-mont. N_2 adsorption isotherms of K10 and V-K10 show that their large surface areas result mainly from mesopores with a pore size distribution and an average pore diameter of 54–65Å, whereas microporosity remains negligible in both dried and calcined V-mont and V-K10.

X-ray diffraction: XRD studies of calcined V-mont show a poor intercalation of vanadium species (spacing of about 5Å) (Fig. 3). This result is in good agreement with the relatively low BET surface area (Table 1). In fact, the vanadium species are mainly anchored to the sheet surface of the clay. For this reason we used another type of montmorillonite, K10, with a deformed and broken layered structure, in order to obtain a better anchorage of vanadium species dispersed on the surface. On thermal treatment in air, a partial transformation of vanadium species to a crystalline new phase (probably clusters of vanadium oxide) occurred as shown by XR diffraction (see Fig. 3b).

EPR spectroscopy: In order to gain some insight into the location and the nature of the vanadium centres, EPR investigations, described in detail elsewhere,[6] have been undertaken. Both dried samples, V-mont and V-K10, show a signal typical of V(IV) $3d^1$ centres with eight line hyperfine patterns due to the interaction of the unpaired electron with the ^{51}V nucleus (I=7/2). The spectra are very similar to those obtained by Montes *et al.*[7] at 77K, showing a monomeric vanadyl (VO^{2+}) species, with g values and hyperfine coupling constants (listed in Table 2), characteristic of a square pyramidal structure with approximate axial symmetry. The spectrum of dried V-mont is shown in Fig. 4a as an example.

The spectra have a well-resolved hyperfine structure but the baseline is not horizontal, which indicate another paramagnetic vanadium species observed by a superimposed broad singlet (marked with a dashed line), due to a strong interaction of vanadium species, which are likely dimeric or polymeric vanadyl units.[6]

The spectra of tetrahedrally coordinate V^{4+}, exhibit different parameters (V^{4+} in $ThGeO_4$ exhibits[7] $g_{//}$=1.831, $g_\perp$ = 1.980 and $A_{//}$ = 191G, $A_\perp$ = 35G), with a smaller coupling constants and are detected only at 77K.[8] As our spectra recorded at 77K and 298K are identical, with a lower intensity of signal at 298K, tetrahedral symmetry of the V^{4+} environment should be discarded.

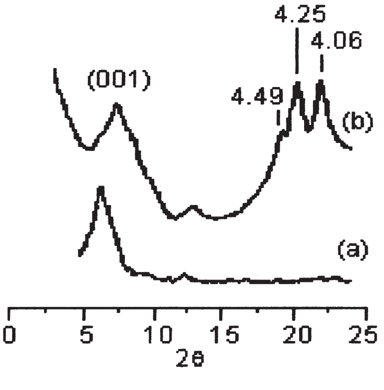


Fig. 3 XRD patterns of calcined natural montmorillonite (a) and V-mont (b) at 573K.

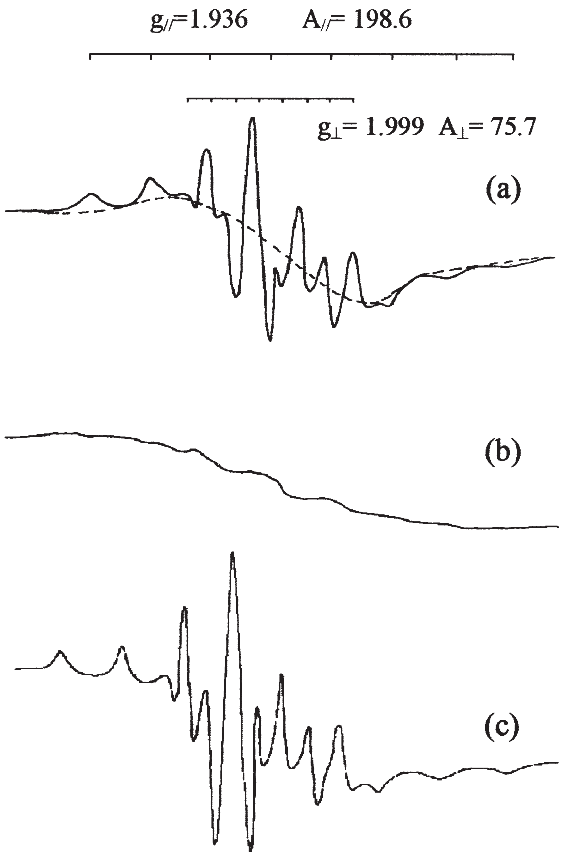


Fig. 4 EPR spectra of V-mont dried at 383K (a), calcined at 573K (b) and after alcohol adsorption on calcined sample at 573K (c).

On calcinations of V-K10 and V-mont samples in air at 573K, both did not exhibit any EPR spectra either at 298 or 77K (Fig. 4 shows the case of calcined V-mont as an example). The V^{4+} ions are probably oxidised to V^{5+} (d^0). On reducing the both calined samples V-mont and V-K10 with adsorbed organic molecules such as alcohol, the typical spectrum of V^{4+} reappeared (Fig. 4 shows the case of calcined V-mont as an example). These results indicate that both V-K10 and V-mont have redox properties and readily change oxidation state between V^{4+} and V^{5+}.

Solid state NMR spectroscopy: ^{51}V NMR data: ^{51}VNMR studies on both V-mont and V-K10 samples 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 V-K10 samples can be interpreted as due to vanadium present in the lattice with tetrahedral oxygen coordination (Fig. 5a). The occurrence of two peaks in the spectrum may be indicative of two vanadium species with different local coordination. The line at around –722ppm can be attributed to an isolated vanadium ion with tetrahedral oxygen coordination (VO_4^{3-}), while the peak at –616ppm can be characteristic of tetrahedric coordination in dimeric state $[O_3V–O–VO_3]^{2-}$. The same peak was detected with pyrovanadates cases, like *e.g.*, $M_2V_2O_7$ (M: Pd, Cd, Zn, Mg).[9,10] On calcination of the V-K10 sample in air at 573K, we note that the intensity of the signal around –722ppm decreases, while the –616ppm signal appears more clearly (Fig. 5b). This modification is probably a result of the increase of the interaction between the vanadium species in the lattice, which is probably favoured by calcinations. The presence of dimeric species in V-K10, could be related to its relatively higher vanadium loading (Table 1). A small peak at –300ppm appears, which can be attributed to a trace of

Table 2 EPR parameters of dried V-K10 and V-mont

Samples	$g_{//}$	$A_{//}$	$g_\perp$	$A_\perp$
V -mont	1.936	198.6	1.999	75.7
V-K10	1.935	197.6	1.997	75.8

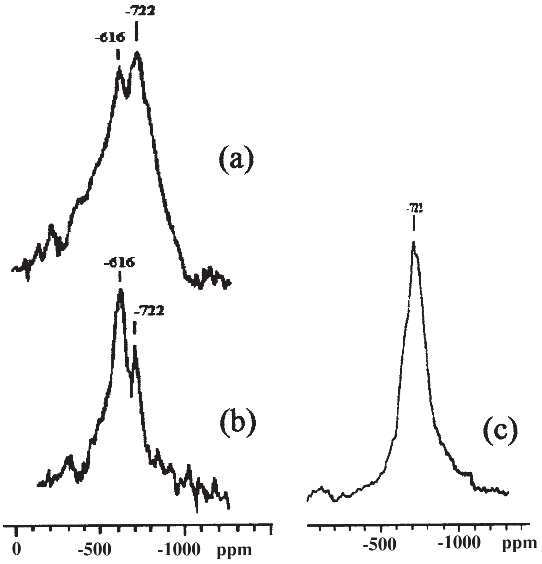


Fig. 5 ^{51}V NMR spectra of V-K10 dried at 383K (a) and calcined at 573K (b) and V-mont calcined at 573K (c).

octahedral vanadium species. It may be concluded that vanadium species in both dried and calcined V-K10 are mainly in tetrahedral coordination.

In the case of V-mont, no V^{51}NMR signal was detected in the dried sample. This can be explain by the presence of vanadium mainly in V^{4+} state which changes upon calcination at 573K to V^{5+} mainly in isolated tetrahedric monomeric species, with a line at around –722 ppm [Figure 5(c)].

^{27}Al and ^{29}Si NMR data: The ^{29}Si and ^{27}Al MAS NMR spectra of natural montmorillonite and K10 have been reported previously.[11] The dried or calcined natural montmorillonite, show only one type of silicon resonance, at –90.9ppm, [Fig. 7 (a)] close to the value reported for Si in clays,[12,13] and an intense peak in the range 2–5 ppm characteristic of octahedral Al, with small peaks at 67-70ppm showing traces of tetrahedral Al [Figure 6 (a)].

The acid treatment induces the appearance of two other resonances, at –109 and –100ppm in the ^{29}Si spectra [Fig. 7 (c)], and an increase of the intensity of the peak at 73ppm in the Al spectra [Fig. 6 (b)]. In their study of aluminosilicates, Magi *et al.*,[13] assigned the signal at –109ppm to silicious impurities associated with the clay, and the peak at –91ppm to Si atoms in the tetrahedral layer of the clay, linked to three other Si atoms and an Al atom in the tetrahedral layer. The peak at -100ppm has been observed and may be explained by the presence of a Q^4 (1Al) structure formed by Si-O-Al^{tet} linkages. This interpretation is supported by the observation of the ^{27}Al NMR signal at 73ppm, which is typical of tetrahedral Al in aluminosilicates.

A ^{27}Al MAS NMR study shows that the chemical shifts corresponding to the different Al species, in both K10 and montmorillonite, are not affected by the presence of vanadium species in the lattice. In fact, the spectra of K10 and montmorillonite are similar to those of V-mont and V-K10 respectively. Thus the interaction of the vanadium species with the Al species seems to be completely discarded.

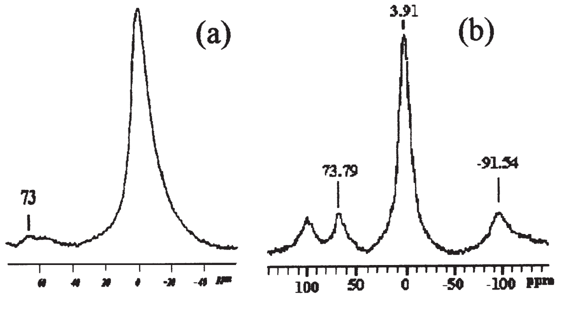


Fig.6 ^{27}Al NMR spectra of dried (at 383K) or calcined (at 573K) natural montmorillonite (a) and K10 (b).

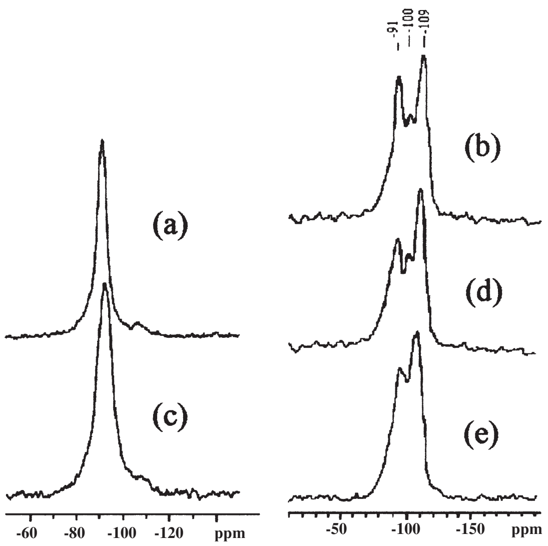


Fig. 7 ^{29}Si NMR spectra of dried (at 383K) or calcined (at 573K) natural montmorillonite (a) and K10 (b), V-mont calcined at 573K (c) and V-K10 dried at 383K (d) and calcined at 573 (e).

On the other hand, the ^{29}Si NMR data obtained for both vanadium-containing systems V-mont and V-K10 suggest that the lattice silicon environnement is in interaction with the vanadium species (Fig. 7 (c) and (d)) According to other studies,[14] the broadening and the displacement of the lines in the spectrum, notably the resonance around –91ppm, can be an indirect indication of the distribution of the vanadium in the lattice. This effect is more pronounced in samples calcined at 573K, which can be due to the increasing interaction between the vanadium and the Si species with increasing calcination temperature [Fig.7 (e)]. No distinct line attributable to V-O-Si sites was observed.

The location of vanadium in the lattice could be suggested also from IR study. In both samples V-K10 and V-mont, the spectra, which result from the subtraction of the spectrum of the solid without vanadium from that with vanadium, show a band at around 950cm^{-1}. This band has been attributed to a V-O-Si vibration due to the presence of vanadium in the lattice.[15] This attribution, is certainly supported by ^{29}Si NMR study.

Catalytic properties: The application of both systems in the epoxidation of allylic alcohols was studied only with samples calcined at 573K. From previous studies[16] on the epoxidation of olefins, it was suggested that the compounds of the metals in their highest oxidation states [Mo(VI), W(VI), V(V), Ti(IV)] are the actual epoxidation catalysts. According the EPR results, vanadium present in samples calcined at 573K, is mainly in the (V) oxidation state.

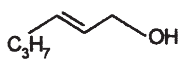
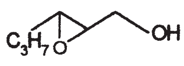
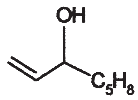
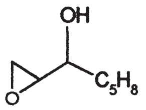
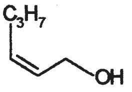
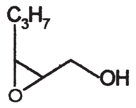
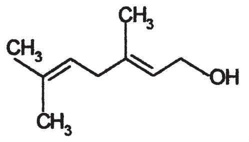
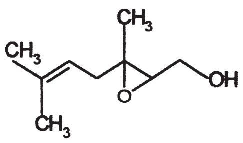
The results summarised in the Table 3, show clearly the higher catalytic activity of V-K10 in epoxidation reaction compared to the V-mont one. V-K10 remains more active than V - mont, even with the use of 40 mg of this last material (Table 3 (entry 1)). In fact, the natural montmorillonite has a regular layered structure, while K10 develops a higher surface area which improves the dispersion of active vanadium species accessible for the complexation with the reactant and oxidant.

In order to more understand and to assume the mechanism of the vanadium epoxidation reaction of allylic alcohol, the study of the TBHP and allylic alcohol adsorption on the catalyst, was followed by EPR spectroscopy.

When the calcined samples were treated with TBHP (*tert*-butylhydroperoxide) and dried in a vacuum at room temperature, EPR spectra were obtained, characterised by the spectroscopic factors: g_1=2.032; g_2= 2.010 and g_3= 2.001 (Fig. 8a. shows the case of calcined V-mont as an example). The signal may result from the presence of tBuOO· species, stabilised by vanadium (V),which lead to the formation of tert-butyl hydroperoxide-vanadium intermediate (see Fig. 10. species (1)).

Adsorption of allylic alcohol on calcined samples, lead to a signal with eight hyperfine lines, which indicate the reduction of V^{5+} to V^{4+} (Fig. 8b shows the result with calcined V-mont as an example). With the mixture of allylic alcohol and TBHP adsorption, the same signal that in the case of TBHP adsorption, was obtained, and after desorption for 2h in vaccum at room temperature, a reduction of

Table 3

Entry	Substrate	Product	$V_0.10^3$mol/1/min		Epoxide yield/%	
			V-mont	V-K10	V-mont	V-K10
1			0.798 1.100*	2.680	30.75 32.35*	32.50
2			0.230	0.490	20.50	23.77
3			0.150	0.204	09.75	10.55
4			06.53	1.754	25.75	27.76

The epoxidation reaction was performed on 7mmol allylic alcohol in dry toluene using 25mg of catalyst (calcined at 573K) and 4mmol of azeotropically-dried TBHP (tert-butylhydroperoxide) in dichlomethane at 338K for 5h. The reaction was periodically monitored by gas chromatography (IGC 120 FL). All products synthesised were analysed by ^{1}H and ^{13}C NMR spectroscopy. *Values obtained using 40mg of catalyst.

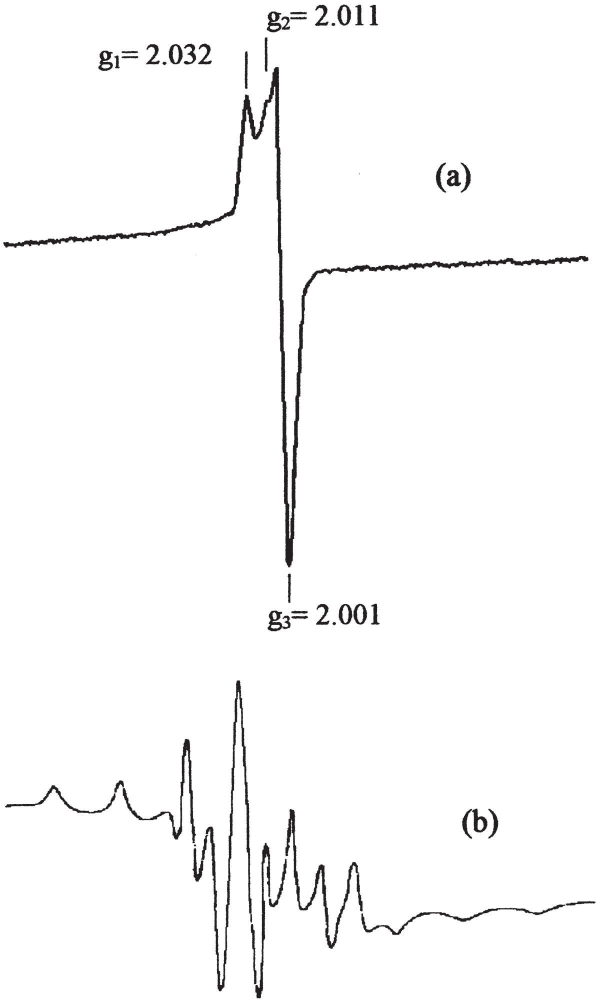


Fig. 8 EPR spectra of V-mont calcined at 573K impregnated with TBHP (a) and with allylic alcohol (b).

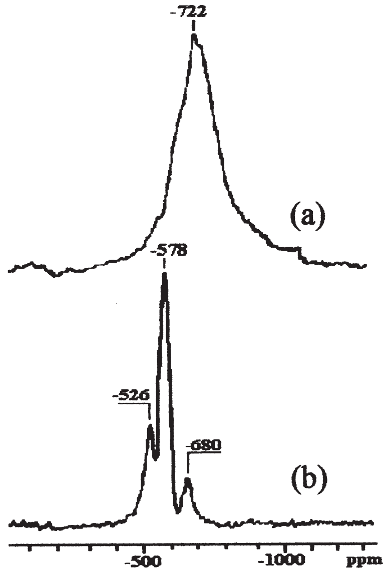


Fig. 9 ^{51}V NMR spectra of V-mont calcined at 573K (a) and impregnated with TBHP (b).

V^{5+} to V^{4+} was obtained with a hyperfine structure. This can be taken as an indication that TBHP is an efficient competitor of allylic alcohol in binding to vanadium. It may be concluded, that the tert-butylhydroperoxide-vanadium intermediate is first formed and then reacts with alcohol.

This intermediate can be also studied using ^{51}VNMR (see Figure 9). When V-mont, calcined at 573K, was impregnated at room temperature with a solution of TBHP in dichloromethane, three relatively sharp peaks appeared, while the broad signal nearly vanished. Apparently, the tetrahedral species react with TBHP. According to the spectrum obtained with precursor solution of VCl_3 in *t*BuOH, we can tentatively ascribe the resonances at –526ppm and –680ppm to framework-bound *tert*-butoxy (V-O-*tB*u) species and those found at –600ppm to framework-bound tert-butyl peroxo species (V–O–O–*tB*u).

Taking in account these results of TBHP and allylic alcohol adsorption on the catalyst surface, it may be assumed that the activity of V-mont and V-K10 in this reaction result from the site isolation of

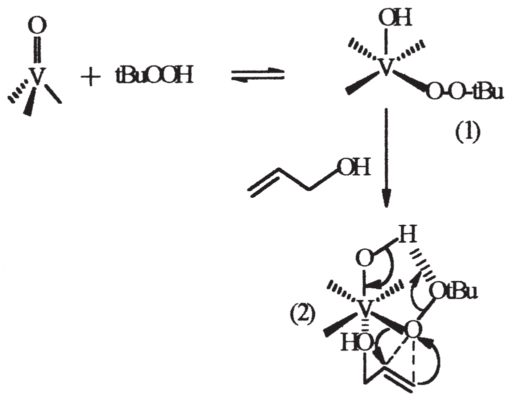


Fig. 10

vanadia centres, which may be vanadyl species in their highest oxidation state (V=O)$^{3+}$. The vanadium in a low oxidation state is rapidly oxidised by *tert*-butylhydroperoxide to its highest oxidation state.

A mechanism can be postulated to explain the vanadium epoxidation reactions of allylic alcohols. It assumes that the *tert*-butylhydroperoxide-vanadium intermediate, which forms first, has to further complex with the allylic alcohol, before the double bound is epoxidised. The geometry of the intermediate complex renders [see Fig. 10. species (2)] the peroxidic oxygens more electrophilic and, hence, more liable to attack by the allylic double bond.

Furthemore, the structure effect of allylic alcohols on the catalytic activity was studied, in order to learn more about the mechanism. In fact, the results summarised in Table 3, show a remarkable regioselectivity; the reaction is limited to the allylic double bonds as evidence in entry 4, giving exclusively mono-epoxide. However, calcined V- K10 and V-mont are less reactive towards terminal allylic alcohol as shown in entry 2 compared to the alcohol in entry 1, but is not passive, as it was indicated in previous studies reported by Choudary *et al.*[17] In fact, the presence of an alkyl group on the double bond renders the allylic double bond more nucleophilic to attack the peroxidic oxygens. For steric effect, we found that alcohol in entry 3 is less reactive than alcohol in entries 1 and 2. In fact, its geometry hinders the complexation with TBHP and vanadium centre, which is not easily accessible. This experimental observation is consistant with the heterolytic mechanism previously postulated.

Conclusion

Two types of vanadium-containing montmorillonite were synthesized and characterised by a variety of physico-chemical techniques. After calcination the vanadium was present in both systems in tetrahedral oxygen coordination and could be reversibly transformed between V^{4+} and V^{5+} states, and in interaction with the lattice silicon environment. In the V-K10 case, the large surface area appears a favourable factor for good catalytic properties in the epoxidation of allylic alcohol compared to the V-mont case. From the adsoption study with TBHP and allylic alcohol, it is assumed that the activities of V-mont and V-K10 in this reaction result from the site isolation of vanadia centres, which may be vanadyl species in their highest oxidation state (V=O)$^{3+}$ formed via the tert-butyl hydroperoxide-vanadium intermediate.

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