

A Study of V-Pillared Layered Double Hydroxides as Catalysts for the Epoxidation of Terpenic Unsaturated Alcohols

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Received July 10, 2000; revised October 13, 2000; accepted October 13, 2000; published online February 13, 2001

Mg,Al-Layered double hydroxides (LDHs) are pillared with vanadium under mildly acidic conditions. Via XRD, Raman, and IR characterization, it is confirmed that the material is a phase-pure LDH with decavanadate ($V_{10}O_{28}^{6-}$) anions between the brucite sheets. This V_{10} -LDH has the highest activity for the epoxidation of geraniol when used with *tert*-butyl hydroperoxide as the oxidant in anhydrous toluene. In a series of tests, the possible release of catalytically active dissolved V from the catalyst is investigated. Under all conditions tested, V_{10} -LDH behaves as a heterogeneous catalyst, in contrast with some other tested V-containing materials (e.g., VAPO-5, or V in a siliceous matrix). Regioselectivity in the epoxidation of geraniol evidences the coordination of the alcohol group of geraniol on the active V center. Finally, it is demonstrated that the V_{10} -LDH catalyst can be applied to the epoxidation of a series of allylic and homoallylic alcohols, mostly of terpene origin.

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Key Words: vanadium; layered double hydroxides; geraniol; terpenes; epoxidation.

INTRODUCTION

Oxidative transformation of fine chemicals is an important target in catalysis, particularly if one desires to obtain products that are free of dissolved metals. Efficient heterogenization routes exist for, e.g., Ti and W, for instance via isomorphous substitution of Ti into molecular sieves, or via exchange of W-based anions (1, 2). However, progress in the design of heterogeneous V catalysts has been less marked. Homogeneous V catalysts are capable of effecting olefin epoxidation, and hydroxylation of alkanes and aromatics, but they are particularly suitable for the epoxidation of allylic and homoallylic alcohols (3–6). The latter reactions are stereospecific and mostly chemoselective, make efficient use of the oxidant, and often proceed under ambient conditions. However, the typical procedure for V-catalyzed epoxidation of allylic alcohols uses up to a few mole percent

of dissolved metal, typically $VO(acac)_2$. Initial attempts to immobilize such V catalysts have focused on V-substituted aluminophosphates, V silicates, or V-pillared montmorillonite (7–10); however, the mixed success of these materials proves that there is a need for the exploration of new, solid catalytic materials.

Several groups have recently reported on the use of metal-exchanged layered double hydroxides (LDHs) as catalysts for liquid phase oxidations (11–13). While LDHs, due to their basic nature, display catalytic activity in the epoxidation of, e.g., unsaturated ketones (14), their use as catalysts for many other reactions requires exchange with a catalytically active anion (15). For instance, tungstate-exchanged LDHs have been used as catalysts for the biomimetic oxidation of bromide anions with H_2O_2 as the oxidant (16); in contact with the same H_2O_2 , molybdate-exchanged LDHs are solid catalysts for generation of dioxygen in the singlet excited state (17). The success of such catalysts is in part due to the infinite oxidative stability of the inorganic support, and to the large anion exchange capacity, which efficiently retains the anions, particularly in solvents of low dielectricity.

Incorporation of V anions into LDHs has been extensively described, and several procedures have been established to pillar LDHs with the polyoxoanion $V_{10}O_{28}^{6-}$ (18–21). However, these materials have received little attention in liquid phase catalysis. There is a report on the aerobic photo-oxidation of isopropanol to acetone catalyzed by $V_{10}O_{28}^{6-}$ -pillared LDH (22).

This paper presents a detailed study of the use of a $V_{10}O_{28}^{6-}$ -pillared LDH (V_{10} -LDH) as a catalyst for the selective epoxidation of allylic and homoallylic alcohols. First, standard characterization techniques are applied to check whether the pillaring is successful, and to evaluate the state of the V in the pillars. Next, optimum reaction conditions are designed for the epoxidation of the typical substrate geraniol. Under the optimized conditions, the heterogeneity of the observed catalysis is critically evaluated with several tests. For the sake of comparison, similar evaluations of other solid V materials are included. These demonstrate

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that V_{10} -LDH is the only material of the set that can be considered as a heterogeneous catalyst. Finally, the applicability of V_{10} -LDH to the epoxidation of a series of terpenic and other (homo)allylic alcohols is demonstrated.

EXPERIMENTAL SECTION

Preparation of Catalysts

LDH. The precursor Mg,Al-LDH was prepared via coprecipitation of Mg^{2+} and Al^{3+} nitrate salts at pH 10. All preparations of LDHs were performed with deionized water that was decarbonated by boiling for 15 min. The typical procedure for synthesis of Mg,Al-LDH has been described elsewhere (23).

V_{10} -LDH. For the synthesis of a decavanadate-pillared LDH (V_{10} -LDH), the suspension of freshly prepared Mg,Al-LDH is used (about 1 g of solid per 100 ml of water), without a drying step (20). The pH of this suspension is brought from 9 to 4.5 with 2 M HNO_3 . Next, 1.0 g of $NaVO_3$ (8.2 mmol) is dispersed in 33 ml of deionized and decarbonated water, and the pH is adjusted to 4.5 with 2 N HNO_3 , resulting in a color change to the characteristic orange of decavanadate. The orange decavanadate solution is then added over 15 min to the LDH suspension, while maintaining the pH at 4.5. After 4 h of stirring at room temperature and centrifugation, a yellow solid is obtained, which is washed five times to remove excess decavanadate. The dry powder is eventually obtained by lyophilization. This direct exposure of the LDH to a decavanadate solution leads to the purest decavanadate-pillared LDH, as indicated by physicochemical data (see below). The V content of this material on a dry weight basis is 21%.

Alternatively, an indirect procedure was used to prepare decavanadate-pillared LDH, via intermediate pillaring with terephthalate anions (V_{10} -LDH(TA)). In this case, the reported procedure of Drezdson was followed (18).

V-LDH. Vanadate-exchanged LDH (V-LDH) was prepared by dispersing 0.2 g of $NaVO_3$ in 15 ml of decarbonated water. One gram of NO_3^- -exchanged Mg,Al-LDH was added, and the suspension was stirred for 24 h at room temperature under N_2 . In contrast with the preparation of V_{10} -LDH, the pH was not adjusted in this case. The solid was extensively washed, and air-dried. In an analogous procedure, a terephthalate-pillared LDH was exposed to $NaVO_3$ (V-LDH(TA)).

VAPO-5. The preparation of this V-substituted aluminophosphate was based on a literature procedure (24). An 8.5 g amount of 85 wt% H_3PO_4 was diluted with 6 g of H_2O . This solution was added to a slurry of 5.5 g of pseudoboehmite in 16 g of H_2O , and the white viscous gel was stirred for 90 min at room temperature. A 0.35 g amount of

V_2O_5 was added to the stirring gel, causing a color change to yellow. After 20 min of homogenizing, 15 ml of tripropylamine was added. The gel was further homogenized for 90 min and finally crystallized for 6 h at 423 K in Teflon-lined autoclaves. The aluminophosphate was isolated and calcined as described by Montes *et al.* (24). The dry material contains 1.4 wt% V.

VO-PVP. One gram of polyvinylpyridine (Reillex 425 polymer) was added to a solution of 0.4 g of $VOSO_4 \cdot 5H_2O$ in 100 ml of ethanol. After overnight shaking, the solid was filtered, extensively washed with ethanol, and dried under vacuum at room temperature (25). The room-temperature, vacuum-dried material contains 7.6 wt% V.

V-SiO₂. To a mixture of 22.3 ml of tetraethyl orthosilicate (0.1 mol) and 0.39 g of Na_3VO_4 (2.12 mmol) in 270 ml of water was added 8 ml of 37% HCl. After 75 h of stirring at room temperature, the solid was filtered, extensively washed with distilled water, and dried at room temperature. Finally, the material was calcined in air by heating to 900 K at 1 K per minute, and maintaining the final temperature for 4 h. A material is obtained with 1.7 wt% V.

V_{10} -Amberlite. To 75 ml of water was added 0.456 g of $NaVO_3$, and the pH was adjusted to 4.5 by addition of a Dowex 50W \times 4 resin. The formation of decavanadate was evidenced by the yellow-orange color of the solution (26). The Dowex was removed by filtration, and to 50 ml of the solution was added 1 g of Amberlite IRA-400. After overnight shaking, the orange polymer beads were isolated by filtration, and extensively washed with distilled water.

Extraction of Decavanadate Species into a Toluene Layer

A solution of sodium decavanadate was prepared as in the previous paragraph, resulting in a 5 mM solution of $V_{10}O_{28}^{6-}$. To 1 ml of this solution (5 μ mol of $V_{10}O_{28}^{6-}$) were added 4 ml of toluene and 0.068 g of tetrapentyl ammonium bromide (180 μ mol). This resulted in complete transfer of the yellow decavanadate into the toluene layer. The solution of decavanadate in toluene (1.25 mM) was used as such in catalytic experiments.

Instrumentation

X-ray diffractograms were recorded with a Siemens D-5000 diffractometer. IR spectra were recorded with KBr pellets, using a Nicolet 730 spectrometer. For Raman spectroscopy, a Bruker Equinox 55-FRA106/S apparatus was employed, with excitation in the near infrared, and an irradiation power between 50 and 100 mW. Visible spectra were recorded with a Perkin Elmer spectrophotometer. Elemental analyses were performed with inductively coupled plasma (Bodemkundige Dienst van België) after calcination of the weighed sample and dissolution in acid.

Catalytic Reactions and Product Analysis

Reactions were started by addition of the oxidant (H_2O_2 , aqueous $t\text{BuOOH}$, or 5 M $t\text{BuOOH}$ in decane, Aldrich) to a magnetically stirred suspension of the substrate and the catalyst in toluene. Products were analyzed on an HP chromatograph with a 60 m CP-Sil 5 column. Authentic epoxides were prepared with *m*-chloroperbenzoic acid as the stoichiometric oxidant, or using a homogeneous $\text{VO}(\text{acac})_2$ catalyst (1–5 mol %) with $t\text{BuOOH}$ in toluene.

Materials

All products were purchased in the highest grade available and used as such: 35% H_2O_2 , cinnamyl alcohol, H_3PO_4 (85%), and *tert*-butyl hydroperoxide (70% solution in water) (all from Akros); (-)-carveol, (*R*)-(-)-carvone, citronellol, crotyl alcohol, 2-cyclohexen-1-ol, geraniol, isophorol, (1*R*)-(-)-myrtenol, nerol, (1*R*)-(-)-noponol, (*S*)-(-)-perillyl alcohol, (*S*)-*cis*-verbenol, (1*S*)-(-)-verbenone, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *tert*-butyl hydroperoxide (5.0–6.0 M solution in decane), and Amberlite IRA-900 (all from Aldrich); (-)-isopulegol, (-)-*trans*-pinocarveol, tetraethyl orthosilicate, tripropylamine, vanadyl acetylacetonate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaVO_3 , and Dowex 50W \times 4 (Fluka); and $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, V_2O_5 , and HCl_{conc} (Merck).

RESULTS AND DISCUSSION

Characterization of the V_{10} -LDH Catalyst

XRD. X-ray diffraction is the easiest method to monitor the spacing of the brucite layers in layered double hydroxide type materials. For the V_{10} -LDH material prepared by direct exposure to decavanadate anions, reflections are observed at 10.2, 5.89 (006), and 3.92 Å (009) (Fig. 1a). As the first reflection is somewhat broadened, it is most appropriate to calculate an average basal spacing $c/3$ from the

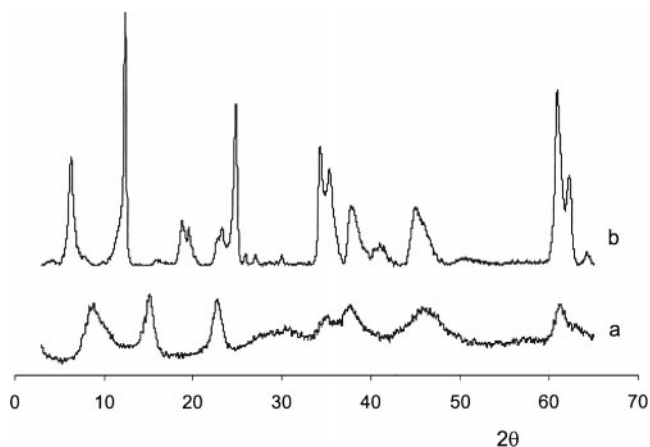


FIG. 1. X-ray patterns of (a) V_{10} -LDH and (b) terephthalate-pillared LDH.

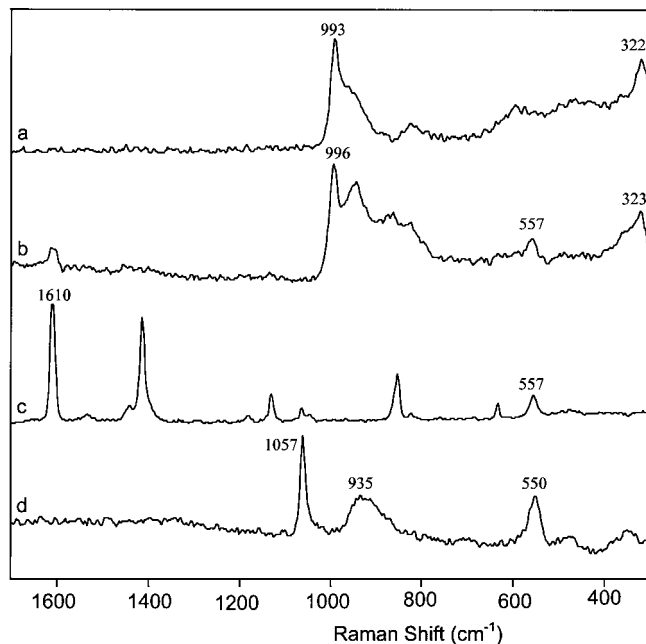


FIG. 2. Raman spectra of (a) decavanadate-pillared LDH, prepared by direct exposure of an LDH to a decavanadate solution (V_{10} -LDH), (b) decavanadate-pillared LDH, prepared by exposure of a terephthalate-pillared LDH to decavanadate (V_{10} -LDH(TA)), (c) terephthalate-pillared LDH, and (d) vanadate-LDH, prepared by exposure of an LDH to NaVO_3 without pH adjustment.

positions of the second and the third reflections. The value $c/3 = 11.8$ Å is in excellent agreement with values reported in the literature (18, 19, 22).

Alternatively, samples were prepared by intercalation of terephthalate anions, and subsequent intercalation with decavanadate anions. For the terephthalate-intercalated sample, there are reflections at 14.07, 7.19, and 4.71 Å (Fig. 1b). The resulting $c/3$ value of 14.2 Å corresponds to a perpendicular orientation of the terephthalate anions between the brucite layers (18, 19). Subsequent exposure of the terephthalate-intercalated LDH to a decavanadate solution results in complete phase transformation. The new material has reflections at 10.6, 5.86, and 3.94 Å, which is in close agreement with the structure obtained by direct exposure of the LDH to decavanadate (*vide supra*).

For all samples, the detection of the (110) plane at 1.52 Å proves that the layered double hydroxide structure of the material is maintained. Moreover, the characteristic reflections of carbonate-containing LDHs (e.g., 7.6 Å) were not observed, indicating that major CO_2 contamination was successfully avoided during synthesis.

Vibrational Spectroscopy

Raman. In order to characterize the nature of the interlayer anions, and especially the state of the V, Raman spectra were recorded (Fig. 2). In the Raman spectra of most LDH samples, a peak at 557 cm^{-1} can be assigned to

the lattice vibrations of the brucite octahedral layers (23). Raman data are particularly useful to distinguish between such species as VO_4^{3-} , $\text{V}_2\text{O}_7^{4-}$, $\text{V}_4\text{O}_{12}^{4-}$, and $\text{V}_{10}\text{O}_{28}^{6-}$ (27–29).

In the Raman spectrum of V_{10} -LDH, prepared by direct exchange of an LDH with an acidified V solution, decavanadate is the dominant species, as evidenced by peaks at 993 and 322 cm^{-1} , and a shoulder at 965 cm^{-1} (Fig. 2a). A highly similar spectrum is observed for aqueous vanadate at a pH between 3 and 6 (27). Additional decavanadate peaks are observed at 600 and 465 cm^{-1} . Only the minor peak in the spectrum at 827 cm^{-1} seems somewhat shifted from the reported value for decavanadate (840 cm^{-1}).

The terephthalate-intercalated LDH has characteristic vibrations of the aromatic carboxylate anion at 3075, 1610, 1413, 1130, 855, and 634 cm^{-1} (Fig. 2c). After intercalation with decavanadate (V_{10} -LDH(TA)), a small amount of residual terephthalate was observed in some cases, as evidenced by the subsistence of, for instance, the 1610 cm^{-1} peak (Fig. 2b). The most intense peaks of V_{10} -LDH(TA) can be assigned to intercalated decavanadate (996, 963, 833, and 323 cm^{-1}). Obviously, incomplete exchange of terephthalate by decavanadate is not a problem when the V_{10} -LDH is prepared by direct exposure of the LDH to decavanadate. Hence, it seems that the direct procedure leads to purer samples than the indirect method via terephthalate intercalation.

For comparison, Fig. 2 also includes the Raman spectrum of the vanadate-exchanged V-LDH material, which was obtained without acidification (Fig. 2d). Apart from a strong and a weak nitrate vibration at 1061 and 710 cm^{-1} , respectively, the major band is observed at 935 cm^{-1} , together with weak bands at 474 and 352 cm^{-1} . This spectrum matches that of aqueous vanadate solutions at a pH between 8 and 11, and corresponds to cyclic species $(\text{VO}_3)_n^{n-}$, with n at least 3, in which VO_2 units are linked by $-\text{O}-$ bridges (27).

IR. IR spectra are in general less useful for the study of these LDH samples, since the LDH structure itself strongly absorbs below 1000 cm^{-1} . For V_{10} -LDH, the only band that can be assigned to V species is located at 960 cm^{-1} , which is the frequency of dissolved decavanadate at pH 4.5 (27). In the IR spectrum of V_{10} -LDH(TA), some residual terephthalate may be observed at 1405 and 1567 cm^{-1} , in addition to the decavanadate $\text{V}=\text{O}$ stretching vibration at 960 cm^{-1} . Hence, there is full agreement between the Raman and IR data.

Summarizing, the physicochemical evidence proves that $\text{V}_{10}\text{O}_{28}^{6-}$ is the prevailing anion when the LDHs are exposed to vanadate solutions at pH 4–5, whether the LDH has been first pillared with terephthalate or not.

Optimization of the Reaction Conditions with V_{10} -LDH and Comparison with Other Decavanadate Catalysts

Several sets of reaction conditions were tested, with geraniol as a model substrate and V_{10} -LDH as the cata-

TABLE 1

Optimization of the Reaction Conditions in the Epoxidation of Geraniol with V_{10} -LDH as the Catalyst^a

Entry	Solvent	Oxidant	Time, h	Conversion, %	Selectivity, % ^b
1	Dioxane	H_2O_2 , 50%	24	9	39
2	Dioxane	tBuOOH, 70%	4	4	55
3	CH_3CN	tBuOOH, 70%	4	28	96
4	Toluene	tBuOOH, 70%	4	59	98
5	Toluene	tBuOOH, decane	4	95	97
6 ^c	Toluene	tBuOOH, decane	34	3	31

^a Conditions: 1 mmol of geraniol, 1.1 mmol of oxidant, 20 mg of catalyst, 2 ml of solvent, 293 K. Conversion of geraniol in %.

^b Selectivity = $100 \times (\text{moles of epoxide formed}) / (\text{moles of geraniol converted})$. Except for entry 6, the ratio (2, 3)/(6, 7) epoxide is at least 50. The main side product is geraniol.

^c No catalyst; (2, 3)/(6, 7) epoxide = 1.

lyst (Table 1). A reaction with H_2O_2 resulted in poor conversion and low epoxide selectivity. Better results were obtained with tBuOOH, even if the reaction outcome depends markedly on the solvent used. With 70% tBuOOH in water as the oxidant, dioxane was not an effective solvent, while better results were obtained in acetonitrile and particularly in toluene (entries 2–4). However, the best yield and selectivity are obtained when 5 M tBuOOH in decane is used as the oxidant, in toluene as the solvent (entry 5). The chemoselectivity is excellent, with minimal formation of geraniol. Moreover, the regioselectivity for the formation of the 2,3-epoxide is high (>98%). Hence, it seems that the V_{10} -LDH is particularly effective if anhydrous conditions are applied.

For comparison, an LDH was tested in which the decavanadate was introduced after first pillaring with terephthalate (V_{10} -LDH(TA)). Eventual conversions and selectivities are practically indistinguishable from those obtained with V_{10} -LDH, prepared by direct pillaring (Table 2, entries 1 and 2). Both catalysts fully preserve their characteristic yellow color during and at the end of the reaction; the filtrate is completely colorless. In contrast with the V_{10} catalysts, low conversions and selectivities are obtained if the vanadate is introduced on an LDH support without acidification (Table 2, entries 3 and 4).

Decavanadate, anion exchanged on an Amberlite, was used under the same conditions as the V_{10} -LDH. The general course of the reaction is similar to that with V_{10} -LDH: the reaction starts without any induction period, and the 2,3-epoxide is the main product. However, much more time is needed to reach even modest conversion levels (Table 2, entry 5). It was noted that the yellow color of the decavanadate-loaded beads was preserved during the reaction of the V_{10} -Amberlite catalyst.

Finally, a solution of decavanadate anions, solubilized in toluene by ion pairing with tetrapentyl ammonium cations, was used as a catalyst, with a geraniol:V ratio of 100, under

TABLE 2
Epoxidation of Geraniol with Solid V Catalysts^a

Entry	Catalyst	Conversion, %	Epoxide selectivity, %	Other products (selectivity, %)
1	V ₁₀ -LDH	80	97	Geraniol (1)
2	V ₁₀ -LDH(TA)	86	98	Geraniol (1)
3	V-LDH	4	77	Geraniol (20)
4	V-LDH(TA)	8	0	Geraniol (100)
5	V ₁₀ -Amberlite ^b	15	98	Geraniol (1)
6	VO-Amberlyst 15 ^c	64	26	Geraniol (2), products of acid rearrangement (72)
7	VO-PVP	95	97	Geraniol (2)
8	VAPO-5 ^d	97	97	Geraniol (1)
9	V-SiO ₂ ^d	85	80	Geraniol (3)

^aGeneral reaction conditions: 1 mmol of geraniol, 1.1 mmol of tBuOOH in decane, 15 mg of catalyst, 2 ml of toluene, 293 K, 4 h (unless stated otherwise).

^bWith 30 mg of catalyst.

^cPrepared by exchange of commercial Amberlyst-15 (in the H⁺ form) with excess VOSO₄.

^dWith 60 mg of catalyst.

conditions that are otherwise identical to those of the heterogeneously catalyzed reactions. In this case, the visible spectrum of the solution was monitored in parallel to the progress of the reaction. The yellow-colored decavanadate has intense absorption between 400 and 500 nm. Remarkably, this decavanadate solution initially displays hardly any activity. When the visible spectrum indicates that at least 50% of the decavanadate anions have disappeared (after 4 h), the reaction suddenly starts (Fig. 3). Thus, surprisingly, the catalytic properties of quaternary ammonium-solubilized decavanadate are quite different from those of

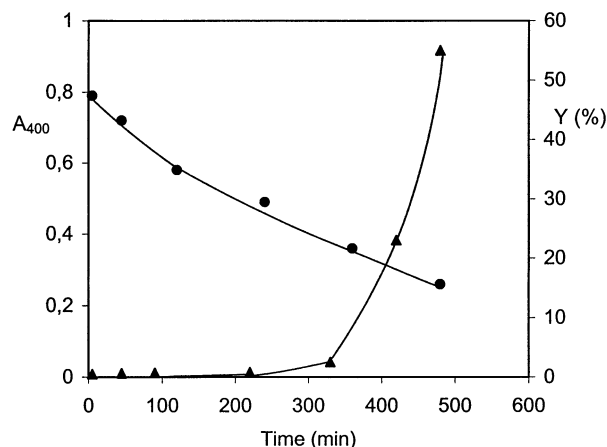


FIG. 3. Epoxidation of geraniol, catalyzed by decavanadate, solubilized by (C₅H₁₁)₄N⁺ in toluene. Evolution of the absorbance at 400 nm (A₄₀₀; ●) and the 2,3-epoxygeraniol yield (Y, %; ▲) as a function of time. Conditions: 1 mmol of geraniol, 1.1 mmol of tBuOOH, 5 M in toluene, 1 μmol of decavanadate, 2 ml of toluene, room temperature.

decavanadate, immobilized by ion exchange on an organic or inorganic solid.

Comparison of a Series of Solid V Catalysts

Table 2 gives a comparison of various solid organic and inorganic V catalysts for the epoxidation of geraniol. With VOSO₄ · H₂O as a V source, VO²⁺ was introduced by coordinative bonding on polyvinylpyridine (VO-PVP) and by ion exchange on the acid cation exchanger Amberlyst 15. With the latter material, residual acidity lowers the epoxide selectivity (entry 6); an excellent epoxide yield was obtained with VO-PVP (entry 7).

Other solids that are effective in the epoxidation of geraniol are the crystalline V-substituted aluminophosphate (VAPO-5, entry 8), and a silica-containing dispersed V^V prepared via a sol-gel process (V-SiO₂, entry 9). A larger weight of catalyst was used in the latter two cases, since the V content of these solids is lower (1.4 wt% V for VAPO-5, and 1.7 wt% V for V-SiO₂, vs 7.6 wt% V for VO-PVP, and 21 wt% V for V₁₀-LDH). Only a meticulous evaluation of the heterogeneous nature of the observed catalysis can reveal the true value of these materials as heterogeneous catalysts.

Stability of the V Under the Reaction Conditions

Different methods were applied to determine whether the catalytic activity was due to homogeneous or really supported species. The catalysts under scrutiny were V₁₀-LDH, VAPO-5, VO-PVP, and V-SiO₂. The optimized conditions for the V₁₀-LDH catalyst were applied, i.e., anhydrous tBuOOH (0.55 M) as the oxidant in toluene, with geraniol (0.5 M) as the substrate.

In the first type of experiment, the role of dissolved vanadium was studied by splitting the reaction suspension at a conversion level between 10 and 20%. Next, the progress of the reaction was monitored in the remaining suspension and in a filtrate, obtained by low-speed centrifugation and filtration over a standard HPLC filter. An example of such an experiment is shown in Fig. 4, for the reaction of geraniol with tBuOOH over V₁₀-LDH. It is obvious that the progress of the reaction in the clear filtrate is negligible. Moreover, the reaction starts immediately, without any noticeable induction time, and the rate is practically constant up to 20% conversion. This indicates that the catalytic activity is not due to slow dissolution of the V species, since this would entail a gradually increasing reaction rate. A practically identical result is obtained when crotyl alcohol is used as the substrate. Thus, the type of allylic alcohol does not affect the stability of the V in V₁₀-LDH. For the other vanadium catalysts, slight to substantial increases in geraniol conversion were observed after solid-liquid separation, and other heterogeneity tests were applied.

In the second test, the solid catalysts were pre-exposed to the oxidant in the absence of an allylic alcohol. Thus,

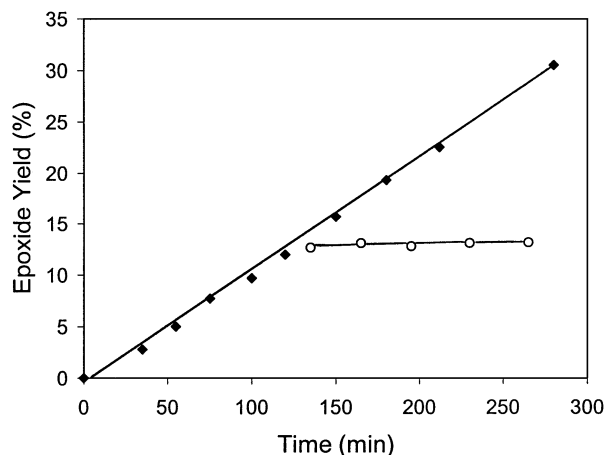


FIG. 4. Heterogeneity test in the epoxidation of geraniol with V_{10} -LDH (2 mmol of geraniol, 2.2 mmol of tBuOOH, 8 mg of catalyst, 4 ml of toluene, 293 K). After 120 min, catalyst was removed from half of the reaction suspension. Reaction progress in the filtrate (○) was then compared to that in the suspension (◆).

after 2 h of stirring at room temperature in a solution of tBuOOH in toluene, the catalyst was removed by centrifugation. Next, allylic alcohol was added to the supernatant, and the conversion was monitored ("pre-exposure" in Table 3). On the other hand, the recovered catalysts were dried, and subjected to a short treatment under vacuum (333–383 K) in order to remove adsorbed organics. The oxidant-exposed catalyst was eventually used in a regu-

lar reaction, and was compared to a fresh material. This test reveals particularly clear results. With V_{10} -LDH, pre-exposure to oxidant does not affect the activity of the solid, while the solution contains only a hardly perceptible activity, comparable to the background reaction without catalyst. However, pre-exposure to the oxidant causes an at least 50% reduction of the activity of the VAPO-5, VO-PVP, and V-SiO₂. Moreover, in the latter three cases, the filtrate has an appreciable activity.

In the third approach, a regular reaction was conducted. At the end of the reaction, the catalyst and the clear solution were separated by centrifugation. The various catalysts were dried (6 h at 383 K for V_{10} -LDH and V-SiO₂; 6 h at 338 K for VAPO-5; 6 h under vacuum at 296 K for VO-PVP); they were then used in the next reaction ("catalyst reuse" in Table 3). With V_{10} -LDH, the original activity of the first run was fully recovered in a subsequent run. With VAPO-5, a mild drying treatment is apparently not sufficient. Only after calcination, the catalytic activity of a reused catalyst approaches that of the fresh material. Finally, major activity decreases were observed for V-SiO₂ and for VO-PVP, even if several regeneration treatments were investigated.

In the fourth and final approach, a reaction was conducted with 1 mmol of geraniol and 1.1 mmol of tBuOOH. The reaction filtrate was collected at the end of a reaction, at over 95% conversion to geraniol epoxide. Next, new aliquots of substrate (1 mmol) and oxidant (1.1 mmol) were added to the clear filtrate ("addition of extra substrate" in Table 3). This addition reduces the overall substrate

TABLE 3

Heterogeneity of Solid V Catalysts in Epoxidation of Geraniol with tBuOOH/Decane as the Oxidant^a

	V_{10} -LDH	VAPO-5	VO-PVP	V-SiO ₂
Regular reaction	81 (3.5 h, 97 S)	27 (3.5 h, 90 S)	93 (3.5 h, 96 S)	91 (9 h, 80 S)
After pre-exposure of catalyst to oxidant and solvent, without substrate				
Filtrate + substrate	6 (24 h, 70 S)	10 (24 h, 71 S)	6 (20 h, 86 S)	26 (20 h, 31 S)
Recovered catalyst ^b + substrate, oxidant and solvent	89 (3.5 h, 96 S)	10 (3.5 h, 90 S)	11 (3.5 h, 87 S)	38 (9 h, 28 S)
Catalyst reuse				
First run	81 (3.5 h, 97 S)	27 (3.5 h, 90 S)	100 (12 h, 96 S)	91 (9 h, 80 S)
Second run	80 (3.5 h, 97 S)	12 (3.5 h, 85 S)	38 (17 h, 93 S)	27 (9, 54 S)
	100 (17 h, 97 S)	25 (3.5 h, 97 S) ^c		
Addition of extra substrate to the filtrate of a completed reaction				
First reaction	81 (3.5 h, 97 S)	96 (3 h, 97 S) ^d	99 (4 h, 97 S)	—
	96 (12 h, 98 S)			—
+Extra substrate (0.55 mol per ml)	48 (7 h, 94 S)	51 (7 h, 92 S)	54 (7 h, 92 S)	—
	51 (24 h, 93 S)	96 (24 h, 95 S)	98 (24 h, 88 S)	—

Note: Conversions are given in % at a given reaction time (h), as well as the selectivity in % (S).

^a Reaction conditions: 0.5 mmol of geraniol and 0.55 mmol of tBuOOH in decane per ml of solvent (toluene). Catalyst concentrations were 6.8 mg/ml (V_{10} -LDH, VAPO-5), 3.6 mg/ml (VO-PVP), and 13.6 mg/ml (V-SiO₂).

^b Catalysts were dried before reuse: 6 h at 383 K for V_{10} -LDH and V-SiO₂; 6 h at 338 K for VAPO-5; 6 h under vacuum at 296 K for VO-PVP.

^c After calcination of the spent catalyst, 4 h at 823 K.

^d With 25 mg of VAPO-5 per ml.

conversion to about 50%. If the reaction is really heterogeneous, the conversion level should stay stationary around 50%. The latter situation is indeed observed with V₁₀-LDH, even if the filtrate is stirred for 24 h at room temperature (Table 3). However, VAPO-5 and VO-PVP clearly fail in this test: over the 24 h after the addition of extra substrate and oxidant, the substrate conversion gradually increases to over 95%.

Summarizing, only in the case of the V₁₀-LDH catalyst can it be proven that the filtrates contain no catalytically active V compounds, while the recovered solid has an activity that matches that of a fresh catalyst. Note that all separations of catalyst and liquor were performed at the same temperature as the reactions themselves (293 K); hence, readsorption of dissolved catalytic species upon cooling of reaction mixtures, which is a frequently encountered problem, is not an issue in the present experiments.

Applicability to Terpene Olefinic Alcohols

Having established that V₁₀-LDH is a truly heterogeneous catalyst for the epoxidation of geraniol, the potential of this catalyst for the epoxidation of a series of other unsaturated alcohols, mostly of terpene origin, was evaluated (Table 4). The standard optimum conditions, as defined in the case of geraniol, viz., tBuOOH in decane, were applied.

High conversions and epoxide selectivities were obtained for a series of terpenic allylic alcohols, such as geraniol, nerol, perillyl alcohol, myrtenol, and *trans*-pinocarveol (entries 1 to 5). For those molecules that contain two double bonds (geraniol, nerol, perillyl alcohol), the epoxidation is highly regioselective and prefers the double bond in proximity of the alcohol group. This proves that also for the heterogeneous LDH catalyst, the mechanism of the V-catalyzed epoxidation probably involves coordination of the allylic alcohol group to the V atom before oxygen transfer takes place. The reactions with geraniol and nerol illustrate that the epoxidations are stereospecific: the reaction with geraniol only yields the 2,3-epoxide of geraniol, and not the isomeric epoxide of nerol. This means that there is no rotation around the double bond during the epoxidation.

Even homoallylic alcohols (C=C-C-COH) are successfully epoxidized with high selectivity, albeit that the yield may be somewhat lower. This is illustrated by the reactions with isopulegol and nopol (entries 6 and 7). If the distance between the alcohol group and the double bond is too large, coordination of the alcohol does not accelerate the epoxidation, and a rather low conversion and epoxide selectivity are obtained, as is observed with β -citronellol (entry 8).

While many allylic alcohols are smoothly epoxidized, a notable exception is verbenol (entry 9). A plausible reason is that coordination of the alcohol to the V is hampered by the bulky carbon skeleton; note that the alcohol group in verbenol is on the same side of the six-membered ring as

the two geminal methyl groups. For other molecules with the 6,6-dimethylbicyclo[3.1.1]heptene structure (myrtenol, *trans*-pinocarveol, nopol), the epoxidation occurs exclusively at the sterically less hindered side of the molecule.

Some nonterpenic allylic alcohols were also subjected to the epoxidation. High conversions with excellent selectivity were obtained for crotyl alcohol and cinnamyl alcohol (entries 10 and 11). While the primary alcohol functions are not oxidized in the presence of a double bond, secondary alcohols are more susceptible to ketonization, particularly the cyclic structures such as carveol or 2-cyclohexen-1-ol. Thus, appreciable amounts of the α,β -unsaturated ketones are formed (entries 12 and 13).

GENERAL DISCUSSION

While the heterogeneous nature of solid V catalysts in liquid phase oxidations has been frequently questioned in the past (7–9), the extensive tests in the present work demonstrate that V₁₀-LDH can be considered as a really heterogeneous epoxidation catalyst. Nevertheless, it is important to emphasize that this claim only pertains to the specified reaction conditions. For instance, we have experienced that a too severe heat treatment of V₁₀-LDH (e.g., overnight at 200°C) results in some leaching when the material is afterward used in a catalytic test, probably because of a minor structural degradation.

V₁₀-LDH has the highest activity with tBuOOH in anhydrous toluene. It is likely that the anhydrous conditions of the reaction prevent extensive hydrolysis of the decavanadate pillars and ensuing V leaching. Apparently, the conditions for maximal activity coincide with those for an optimum heterogeneity. Another important element is the mild reaction temperature. The allylic alcohols are easily epoxidized at room temperature, whereas previous studies of oxidation of, e.g., olefins or aromatics with solid V catalysts often were conducted at temperatures between 60 and 80°C (7–9). At these temperatures, and under aqueous conditions (e.g., with H₂O₂), leaching is more probable than under the mild conditions of our tests.

It is striking that the only material which is really heterogeneous contains polynuclear V. In leaching materials such as VAPO-5 or V-SiO₂, the V can be assumed to be monomerically dispersed. In a decavanadate pillar, each V atom is linked via at least five V–O–V bonds to the rest of the pillar. Apparently, this fivefold bonding sufficiently withstands the conditions of the epoxidation reactions, so that all V is effectively withheld within the structure. A somewhat similar situation is generally accepted to occur with the Ti catalyst TS-1: of the four possible Ti–O–Si links, at least two stay intact during catalytic oxidation reactions with H₂O₂ (1). At contrast, in a material such as V-SiO₂, the binding of the V to the support may be rather loose, and this may facilitate the release of active V species.

TABLE 4
Epoxidation of Terpenic and Nonterpenic (Homo)Allylic Alcohols with V₁₀-LDH^a

Entry	Substrate	<i>t</i> , h	Conversion, %	Main epoxide product	Epoxide selectivity, %	Selectivity, %, aldehyde or ketone
1	Geraniol 	4	95		97 ^b	1 (geranial)
2	Nerol 	24	98		97 ^b	2 (neral)
3	Perillyl alcohol 	14	100		99 ^c	1
4	Myrtenol 	14	97		91 ^d	1 (myrtenal)
5	<i>trans</i> -Pinocarveol 	10	91		87 ^d	1
6	Isopulegol 	14	81		94 ^e	4
7	Nopol 	48	61		90 ^d	2
8	β -Citronellol 	24	25		55 ^e	1
9	Verbenol 	24	14		10	65 (verbenone)
10	Crotyl alcohol 	14	65		100 ^f	—
11	Cinnamyl alcohol 	24	85		100	—
12	2-Cyclohexen-1-ol 	24	28		75	22 (enone)
13	Carveol 	24	64		88 ^g	12 (carvone)

^a Procedure: 1 mmol of olefin, 1.1 mmol, 5–6 M, of tBuOOH in decane, 12 mg of catalyst, 2 ml of toluene, 293 K.

^b (2, 3) : (6, 7) epoxide > 50. Two enantiomeric epoxides (50 : 50).

^c Only the double bond in the ring is epoxidized. The diastereomeric (1, 2) epoxides are formed in a 70 : 30 ratio, see Refs. (31, 32).

^d More than 95% selectivity for the isomer shown.

^e Two diastereomeric epoxides (~50 : 50).

^f *Trans* : *cis* = 28 : 1. Commercial crotyl alcohol contains 4–5% *cis* isomer.

^g Commercial carveol is a mixture of the *trans* and *cis* isomers (Ref. 33). The *trans*-carveol reacts much faster than *cis*-carveol.

The intercalation of decavanadate in the LDH materials provides a unique opportunity to study the catalytic properties of these compounds under anhydrous conditions, with tBuOOH as the oxidant. When homogeneous decavanadate is dissolved as a quaternary ammonium salt in toluene, it displays a very low activity, which may tentatively be ascribed to a too strong wrapping of the decavanadate by the organic cations. Consequently, the peroxide and the substrate have no access to the decavanadate; the reaction only starts after an induction period, when the UV-visible spectrum evidences disappearance of the decavanadate. A similar situation has been observed with P-W Keggin heteropolyanions, which are degraded by a peroxide before they display an appreciable epoxidation activity (30). This contrasts with the behavior of decavanadate, exchanged on an LDH or in an organic resin. Particularly in the LDH, the decavanadate seems well accessible, and the epoxidation starts immediately, without a noticeable induction period.

The results of the epoxidation of a series of allylic alcohols (Table 4) strongly evidence that the alcohol group in the substrate molecule coordinates on the peroxy-V center. This implies that the active V species participates in the reaction with two coordination sites, one for the peroxide activation, and another for the alcohol coordination. Since a V atom is initially bound to the pillar with at least five V–O–V bonds, one or two of these bonds must be broken to enable reaction. Nevertheless, this leaves a sufficient number of V–O–V bonds intact to keep all V within the polyanions, as is firmly substantiated by the heterogeneity tests.

Summarizing, we have proven that under well-defined conditions, decavanadate-pillared LDH is a useful heterogeneous catalyst for selective epoxidation of terpenic allylic alcohols.

ACKNOWLEDGMENTS

We are grateful to Colciencias (A.L.V.), IWT (B.F.S.) and FWO (D.E.D.V.) for fellowships. This work is sponsored by the Belgian Federal Government in an IUAP program, Supramolecular Catalysis.

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