Liquid-phase Epoxidation of Alkenes Using Molecular Oxygen Catalyzed by Vanadium Cation-exchanged Montmorillonite

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Vanadium cation-exchanged montmorillonite can efficiently catalyze the selective epoxidation of various alkenes and the oxygenation of adamantane using molecular oxygen as a sole oxidant.

Epoxidation is one of the most fundamental and important reactions in organic synthesis.[1] Various methods have been developed and exploited, and the search for new environmentally friendly methods using molecular oxygen (O_2) as the sole oxidant has attracted much interest. However, there have been few reports concerning the epoxidation of alkenes using 1 atm of O_2 without the use of reducing reagents.[2]

Montmorillonites (monts) of smectite clays are composed of negatively charged layers and an interlayer with cationic species.[3] The cationic species can easily be replaced by other metal polycations using the cation exchange ability of the interlayer, and the metal cation-exchanged monts have considerable potential as heterogeneous catalysts for various organic transformations.[4] Here, we report the synthesis and characterization of vanadium cation-exchanged mont (V-mont) as well as its performance in catalyzing the epoxidation of various alkenes using 1 atm of O_2 as an oxidant. The V-mont-catalyzed aerobic oxygenation of adamantane via C–H activation is also described.

V-mont was prepared as follows: Na^+-mont, $Na_{0.66}(OH)_4Si_{7.7}(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$ (6.0 g) (Kunipia F, Kunimine Industry Co., Ltd.) was added to 100 mL of aqueous VCl_3 solution (0.025 M). Aqueous HCl (1 mL, 10 M) was added, and the mixture was stirred at 60 °C for 24 h. The resulting slurry was filtered and washed with distilled water, then dried at 110 °C and calcined at 800 °C for 18 h, giving 5.5 g of V-mont (V content: 0.97 wt %). XRD measurement showed that the lamellar structure of the uncalcined V-mont with interlayer space of 2.9 Å was transformed into a card-house structure by the above calcination process.[5]

The height of the pre-edge peak in V K-edge XANES spectrum of the calcined V-mont was similar to that of Na_3VO_4, but differed from that of $VOSO_4$, as shown in Figure 1a.[6] This result showed that the vanadium species existed in a tetrahedral-like geometry. Furthermore, the energy position of the pre-edge peak and the absorption edge for the V-mont were higher than those of $VOSO_4$, suggesting that the oxidation state of the V-mont is 5+.[6] In Fourier transform (FT) of k^3-weighted V K-edge EXAFS, no peaks due to a V–O–V bond, detectable in the spectrum of V_2O_5 at around 2.7 Å, was observed for the V-mont (Figure 1b). The inverse FT of the peak around 1–2 Å was well fitted using two short (1.59 Å) and two long (1.70 Å) V–O bonds. The short V–O distance is associated with a V=O bond, as found in V_2O_5.[7] The above results suggest that a highly dispersed monomeric dioxo V^{5+} species surrounded by four oxygen atoms can be created on the mont.

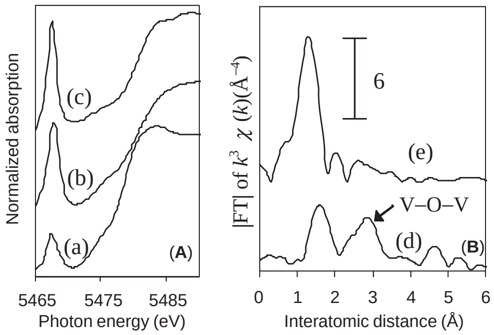
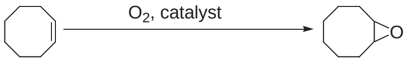


Figure 1. (**A**) V K-edge XANES spectra of (a) $VOSO_4$, (b) V-mont, and (c) Na_3VO_4. (**B**) Fourier transforms of k^3-weighted V K-edge EXAFS for (d) V_2O_5, and (e) V-mont.

Table 1. Epoxidation of cyclooctene catalyzed by metal cation-exchanged monts and vanadium compounds using O_2[a]



Entry	Catalyst	Yield of epoxide/%[b]
1[c]	V-mont[d]	80
2	V-mont[d]	31
3	V-mont[d,e]	trace
4	Fe-mont	trace
5	Mn-mont	trace
6	Mo-mont	trace
7	Ru-mont	trace
8	Na-mont	trace
9	V_2O_5[d]	4
10	V-X zeolite[d]	1
11	V/Al_2O_3[d]	trace
12	$VO(acac)_2$[d]	trace

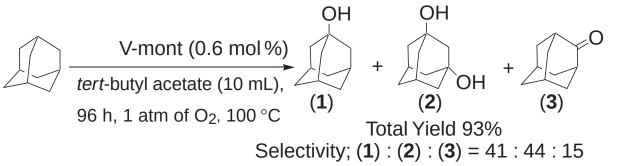
[a]Substrate (3 mmol), catalyst (0.1 g), α,α,α-trifluorotoluene (5 mL), 90 °C, 48 h, O_2 atmosphere. [b]Determined by GC analysis using an internal standard technique. [c]α,α,α-Trifluorotoluene (1 mL), 72 h. [d]V (0.019 mmol). [e]Uncalcined V-mont was used.

Initially, epoxidations of cyclooctene were carried out using various metal-exchanged monts under 1 atm of O_2 in α,α,α-trifluorotoluene solvent,[8,9] as shown in Table 1. Among the catalysts examined, the calcined V-mont proved the most efficient for the epoxidation of cyclooctene (Entry 2). Interestingly, the uncalcined V-mont was found to be less effective (Entry 3). Other vanadium catalysts such as V_2O_5, V-X Zeolite, V-alumina, and $VO(acac)_2$ gave poor results (Entries 9–12). Under optimized reaction conditions, the yield of cyclooctene oxide reached up to 80% with >99% selectivity after 72 h (Entry 1). To the best of our knowledge, this is the first example of selec-

Table 2. Epoxidation of various alkenes by V-mont in the presence of O_2^{a}

Entry	Substrate	Yield of epoxide/%^{b}	Selectivity/%
1	Cyclooctene	80	>99
2^{c}	Cyclooctene	79	98
3^{d}	Cyclooctene	78	98
4	Cyclododecene	40	93
5	Cyclopentene	35	54^{e}
6	2-Octene	21	80^{f}
7	1-Octene	11	85^{g}

^{a}Substrate (3 mmol), V-mont (0.1 g, V: 0.019 mmol), α,α,α-trifluorotoluene (1 mL), 90 °C, 72 h, O_2 atmosphere. ^{b}Determined by GC analysis using an internal standard technique. ^{c}Reuse-1. ^{d}Reuse-2. ^{e}2-Cyclopentene-1-ol was formed. ^{f}Small amounts of octanal was formed. ^{g}Small amounts of decanal was formed.



Scheme 1.

tive liquid-phase epoxidation of cyclooctene using a heterogeneous catalyst with an atmospheric pressure of O_2 as the sole oxidant.[2]

The scope for epoxidation using the V-mont catalyst is summarized in Table 2. This V-mont selectively catalyzed the epoxidation of various kinds of cyclic and linear alkenes with 1 atm of O_2, affording the corresponding epoxides as major products. Upon completion of the epoxidation of cyclooctene, the V-mont was separated from the reaction mixture by simple filtration, and could be reused without any appreciable loss of its high catalytic activity and selectivity (Entries 2 and 3).

Additionally, the above V-mont exhibited high catalytic activity for the oxygenation of adamantane in *tert*-butyl acetate solvent under an atmospheric O_2 pressure, affording 1-adamantanol (**1**), 1,3-adamantanediol (**2**), and 2-adamantanone (**3**); the total yield of oxygenated products reached 93% at 96 h, as shown in Scheme 1.[10] Oxidation did not proceed in the absence of the V-mont under identical reaction conditions. This yield is higher than those reported for other methods of adamantane oxidation with O_2 as a sole oxidant.[11]

The above two oxidation reactions were inhibited by the addition of radical scavengers such as *p-tert*-butylcatechol and 2,6-di-*tert*-butylphenol. Furthermore, the ratio of oxidation at tertiary vs secondary positions in the oxygenation of adamantane was 8.6:1, which is similar to the ratio observed for radical oxidations.[12] These facts suggest that the above oxidations by the V-mont involve a radical oxidation mechanism.[11a,12]

In conclusion, we have developed a highly efficient heterogeneous catalyst system based on monts for the epoxidation with molecular oxygen. This system has the following advantages: (a) the use of 1 atm of molecular oxygen as an oxidant without the need for reducing reagents or radical initiators, (b) high catalytic activity and selectivity, (c) recyclable catalysts, and (d) application to aerobic oxygenation of adamantane via C–H activation. Further studies on mechanistic details and possible extension to other organic syntheses are currently underway.

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References and Notes

1 a) "Modern Oxidation Methods," ed. by J.-E. Bäckvall, Wiley-VCH, Weinheim (2004). b) "The Activation of Dioxygen and Homogeneous Catalytic Oxidation," ed. by D. H. R. Barton, A. E. Martell, and D. T. Sawyer, Plenum, New York (1993). c) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidation of Organic Compounds," Academic Press, New York (1981).

2 There is only one heterogeneous catalyst for liquid-phase epoxidation, which has been applied only to styrene, see: a) Q. Tang, Y. Wang, J. Liang, P. Wang, Q. Zhang, and H. Wan, *Chem. Commun.*, **2004**, 440. Homogeneous catalysts, see: b) Y. Nishiyama, Y. Nakagawa, and N. Mizuno, *Angew. Chem., Int. Ed.*, **40**, 3639 (2001). c) R. Neumann and M. Dahan, *J. Am. Chem. Soc.*, **120**, 11969 (1998). d) R. Neumann and M. Dahan, *Nature*, **388**, 353 (1997). e) A. S. Goldstein, R. H. Beer, and R. S. Drago, *J. Am. Chem. Soc.*, **116**, 2424 (1994). f) M. M. T. Khan and A. P. Rao, *J. Mol. Catal.*, **39**, 331 (1987). g) J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, **107**, 5790 (1985).

3 a) Y. Izumi and M. Onaka, *Adv. Catal.*, **38**, 245 (1992). b) P. Laszlo, *Acc. Chem. Res.*, **19**, 121 (1986). c) T. J. Pinnavaia, *Science*, **220**, 365 (1983).

4 a) T. Kawabata, M. Kato, T. Mizugaki, K. Ebitani, and K. Kaneda, *Chem.—Eur. J.*, **11**, 288 (2005). b) T. Kawabata, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.*, **125**, 10486 (2003). c) T. Kawabata, T. Mizugaki, K. Ebitani, and K. Kaneda, *Tetrahedron Lett.*, **44**, 9205 (2003). d) T. Kawabata, M. Kato, T. Mizugaki, K. Ebitani, and K. Kaneda, *Chem. Lett.*, **32**, 648 (2003). e) K. Ebitani, M. Ide, T. Mitsudome, T. Mizugaki, and K. Kaneda, *Chem. Commun.*, **2002**, 690. f) T. Kawabata, T. Mizugaki, K. Ebitani, and K. Kaneda, *Tetrahedron Lett.*, **42**, 8329 (2001). g) K. Ebitani, T. Kawabata, K. Nagashima, T. Mizugaki, and K. Kaneda, *Green Chem.*, **2**, 157 (2000).

5 After calcination of the V-mont, the diminishing intensity of the (001) diffraction and maintaining of the clay phase are indicative of the transformation into a card-house structure.

6 The V ions in Na_3VO_4 and $VOSO_4$ are known to exist in a tetrahedral coordination and square-pyramidal coordination, respectively, see: J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Haylotte, *Phys. Rev. B*, **30**, 5596 (1984).

7 H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr. Mineral.*, **115**, 110 (1961).

8 Various metal cation-exchanged monts (M-monts) were prepared in a similar way by treatment of Na-mont with aqueous solution of the corresponding metal chlorides. A general procedure for V-mont-catalyzed epoxidation of cyclooctene is as follows: Into a reaction vessel equipped with a reflux condenser and balloon were placed the V-mont (0.1 g, V: 0.019 mmol), cyclooctene (3 mmol), and α,α,α-trifluorotoluene (1 mL). After vigorous stirring of the heterogeneous reaction mixture at 90 °C for 72 h, the catalyst was separated by centrifugation. GC analysis of the supernatant showed an 80% yield of epoxide.

9 With respect to solvents, the use of α,α,α-trifluorotoluene and *tert*-butyl acetate afforded high yields of cyclooctene oxide (80%). The reaction carried out in CH_3CN gave a moderate yield (30%), while toluene, and 1,2-dichloroethane were significantly less effective (<1%).

10 1-Adamantanol was a major product at 48 h. The selectivities of (**1**), (**2**), and (**3**) were 78:4:18, respectively.

11 Product yields for oxygenation of adamantane: a) S. Shinachi, M. Matsushita, K. Yamaguchi, and N. Mizuno, *J. Catal.*, **233**, 81 (2005), vanadium-substituted phosphomolybdates catalyst (84%). b) K. Yamaguchi and N. Mizuno, *New J. Chem.*, **26**, 972 (2002), Ru-substituted silicotungstate catalyst (42%). c) N. Mizuno, M. Tateishi, T. Hirose, and M. Iwamoto, *Chem. Lett.*, **1993**, 2137, Ni and Fe-substituted heteropolyanion catalyst (29%). d) M. M. T. Khan, D. Chatterjee, S. Kumar, and A. P. Rao, *J. Mol. Catal.*, **75**, L49 (1987), Ru-saloph complex catalyst (13%). See: 2C) Ru-substituted polyoxometalate catalyst (57%).

12 a) Y. Ishii, *J. Mol. Catal. A: Chem.*, **117**, 123 (1997). b) Y. Ishii, T. Iwasawa, S. Sakaguchi, K. Nakayama, and Y. Nishiyama, *J. Org. Chem.*, **61**, 4520 (1996).

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