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Simple and Efficient 1,3-Isomerization of Allylic Alcohols using a Supported Monomeric Vanadium-Oxide Catalyst

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The catalytic isomerization of allylic alcohols by the 1,3-transposition of a hydroxy group is an important reaction in organic synthesis.^[1,2] This isomerization has been applied to the industrial production of terpene alcohols, such as geraniol and nerol from linalool. In early studies, the isomerization of allylic alcohols was accomplished by using metal-oxo catalysts, such as trialkyl vanadates^[3] and tungsten-oxo complexes,^[4] operating at high temperatures (>130 °C). Since then, some improvements in the catalytic efficiency have been reported.^[5–14] However, these catalytic systems have a variety of associated problems, including the decomposition of the catalyst,^[10] the formation of byproducts,^[11,12] the requirement for the addition of activators,^[5,6,10] or use of precious metals^[6–9,11,12] and their difficulty in recycling the catalysts.

Heterogeneous catalysts have numerous advantages over homogeneous catalysts in terms of their durability and their facile separation from the reaction mixture and subsequent reusability, as well as their applicability in packed column reactors and multi-step flow reactors. However, despite these advantages, few efficient heterogeneous catalysts have been developed for the 1,3-isomerization of allylic alcohols. The attempted heterogenization of a formerly homogeneous active tungsten species by using polyvinyl pyridine as a support has been reported, but was unsuccessful owing to decomposition of the polymer and leaching of the active metal.^[4] Thus far, there has only been one report of an effective heterogeneous catalytic system, which was based on the use of polymer-bound vanadyl phosphate (PhosphonicS POVO).^[15]

Herein, we report the use of silica-supported monomeric vanadium-oxo species (V/SiO₂) to effectively promote the isomerization of various allylic alcohols under mild reaction conditions, without the addition of any activators.^[16] The V/SiO₂ catalyst can be easily prepared and is highly durable, thus exhibiting excellent reusability without any loss of efficiency.

The V/SiO₂ catalyst was prepared according to an impregnation method.^[17] SiO₂ (3.0 g) was added to an aqueous solution of NH₄VO₃ (8.4 mM). The mixture was stirred at 80 °C for 2 h, followed by evaporation of the water. The obtained slurry was dried overnight at 110 °C and subsequently calcined under a flow of dry air at 500 °C for 5 h to afford V/SiO₂ (V: 1.4 wt.%). V/SiO₂ was characterized by X-ray absorption fine structure (XAFS) spectroscopy. The V K-edge X-ray absorption near-edge structure (XANES) spectrum of V/SiO₂ exhibited an absorption edge at 5480 eV, which was assigned to V⁵⁺ species (see the Supporting Information, Figure S1).^[18] The spectrum also showed a strong pre-edge peak, which was more intense than that of V₂O₅ yet weaker than that of Na₃VO₄, thus suggesting that the V species in V/SiO₂ adopted a distorted tetrahedral structure.^[19,20] The diffuse-reflectance UV/Vis spectrum of V/SiO₂ showed a charge-transfer band at about 250–300 nm, which was assigned to monomeric tetrahedral VO₄ species (see the Supporting Information, Figure S2).^[21] The Raman spectrum showed a peak at 1040 cm⁻¹, which was attributed to the V=O stretching vibration (see the Supporting Information, Figure S3).^[22] These results indicate that vanadium is present on the SiO₂ surface as a monomeric vanadium-oxo species with a distorted tetrahedral structure, which is in good agreement with previous results reported by Tanaka and co-workers.^[21]

Initially, we examined the catalytic activity of V/SiO₂ for the 1,3-isomerization of α -vinylbenzyl alcohol (**1**) in MeCN at room temperature.^[23] Interestingly, V/SiO₂ exhibited pronounced catalytic activity, thereby affording cinnamyl alcohol (**2**) in 73% yield with no byproducts (Table 1, entry 1). A longer reaction time further increased the yield of **2** to 95% (Table 1, entry 2). In sharp contrast to these results, the use of supported vanadium species V/Al₂O₃, V/TiO₂, and V/hydrothermalite^[24] hardly promoted the isomerization (Table 1, entries 8–10). Substituting V/SiO₂ with the previously reported and commercially available heterogeneous V catalyst PhosphonicS POVO resulted in a very low yield of **2** (Table 1, entry 11). In addition, the use of V compounds V₂O₅ and VO(acac)₂, as well as the NH₄VO₃ precursor compound and the SiO₂ catalyst support, all led to poor yields of **2** (Table 1, entries 12–15). These results clearly demonstrate that V/SiO₂ has outstanding catalytic activity for the isomerization reaction. Hence, the immobilization of V on the SiO₂ support clearly resulted in the creation of highly active vanadium species for promoting the isomerization reaction.

Subsequently, the V/SiO₂ catalyst was removed from the reaction solution by filtration once 40% conversion of **1** had been achieved and the stirring of the filtrate was resumed with periodic analysis of the conversion. No further conversion was found after the removal of the catalyst, thus demonstrat-

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Table 1. 1,3-Isomerization of α -vinylbenzyl alcohol by using various vanadium catalysts.^[a]

Entry	Catalyst	<i>t</i> [h]	Conv. ^[b] [%]	Yield ^[b] [%]
1	V/SiO ₂	2	73	73
2	V/SiO ₂	6	98	95
3	V/SiO ₂ (1st reuse)	6	98	97
4	V/SiO ₂ (2nd reuse)	6	95	95
5	V/SiO ₂ (3rd reuse)	6	97	97
6	V/SiO ₂ (4th reuse)	6	97	97
7	V/SiO ₂ (5th reuse)	6	98	95
8	V/Al ₂ O ₃	2	4	2
9	V/TiO ₂	2	2	1
10	V/hydratalcite	2	<1	<1
11	PhosphonicS POVO	2	16	12
12	V ₂ O ₅	2	<1	<1
13	VO(acac) ₂	2	5	4
14	NH ₄ VO ₃	2	2	2
15	SiO ₂	2	<1	<1

[a] Reaction conditions: Catalyst (5 mol%), substrate (0.3 mmol), MeCN (2 mL), Ar atmosphere. [b] Yields were determined by GC with an internal standard.

ing that the isomerization occurred solely at the V species on the solid SiO₂. In addition, inductively coupled plasma atomic emission spectroscopy (ICP-AES) of the filtrate showed no leaching of V into the reaction solution (at a detection limit of 0.1 ppm), thus confirming that the catalyst was heterogeneous. After the isomerization reaction, the used V/SiO₂ catalyst was readily separated from the reaction mixture and was found to be reusable without any loss of efficiency (Table 1, entries 3–7). This result confirmed the excellent durability of the V/SiO₂ catalyst.

Next, we investigated the scope of the V/SiO₂-catalyzed isomerization of allylic alcohols and found that V/SiO₂ exhibited high catalytic activity towards a number of different alcohols, as summarized in Table 2. Secondary aromatic allylic alcohols were successfully converted into their corresponding primary allylic alcohols (Table 2, entries 1 and 3). Notably, the V/SiO₂ catalyst was tolerant of a sulfur-containing heterocyclic alcohol, thus giving the desired isomerized alcohol as the sole product in high yield (Table 2, entry 4), whereas previously reported Re-based complexes were severely poisoned by reaction with sulfur-containing compounds, thus resulting in no product formation. Aliphatic allylic alcohols were also reactive: 1,4-Pentadien-3-ol was readily converted into 2,4-pentadien-1-ol in 78% yield (Table 2, entry 5). In addition, it was possible to obtain tertiary aliphatic alcohols from their corresponding primary or secondary alcohols in good yields (Table 2, entries 6 and 7). The reverse isomerization reactions of 1-octen-3-ol and 2-octen-1-ol both resulted in the same equilibrium distribution of isomers (Table 2, entries 8 and 9).

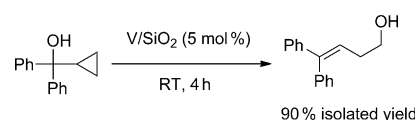
Notably, V/SiO₂ performed well under scaled-up and solvent-free conditions: **1** (2.6 g, 20 mmol) readily underwent the isomerization reaction to afford 2.3 g (88% yield) of **2** (Table 2,

Table 2. Isomerization of various allylic alcohols by using V/SiO₂.^[a]

Entry	Substrate	Product	<i>T</i> [°C]	<i>t</i> [h]	Conv. [%] ^[b]	Yield [%] ^[b]
1			RT	6	98	95
2 ^[c]			40	24	–	88 ^[d]
3			RT	14	93	93
4			40	4	83	82
5			10	12	78	78
6			40	4	83	76
7			0	1	64	64
8			60	16	40	40
9			60	8	60	60
10			80	16	55	55

[a] Reaction conditions: V/SiO₂ (5 mol%), allylic alcohol (0.3 mmol), MeCN (2 mL), Ar atmosphere. [b] Yields were determined by GC with an internal standard. [c] V/SiO₂ (2 mol%), allylic alcohol (20 mmol), solvent-free conditions. [d] Yield of isolated product.

entry 2). Moreover, this catalytic system was found to be applicable to the isomerization of a cyclopropanemethanol derivative into its corresponding homoallylic alcohol, which is a key reaction in the synthesis of some natural products.^[25] In a typical reaction, diphenylcyclopropylmethanol was converted into 4,4-diphenyl-3-buten-1-ol in excellent yield, as shown in Scheme 1.



Scheme 1. V/SiO₂-catalyzed isomerization of diphenylcyclopropylmethanol.

To gain more insight into the high efficiency of V/SiO₂, the relationship between the structure of the active site and the catalytic activity was investigated by following the isomerization of **1** by using V/SiO₂ catalysts with different V loadings. As shown in Figure 1, the catalytic activity of V/SiO₂ increases with decreasing V content in V/SiO₂ over the range 5.1–1.4 wt.%. UV/Vis absorption spectroscopy showed that decreasing V content was also associated with a concurrent rise in the intensity of the absorption bands at 250 and 300 nm, which were attributed to monomeric V species.^[26] Thus this increase in the fraction of monomeric V species has a significant correlation with the high catalytic activity, as shown by

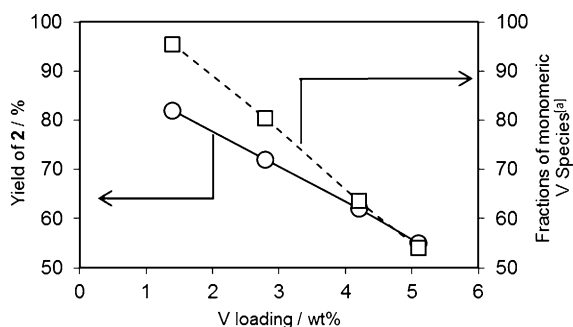
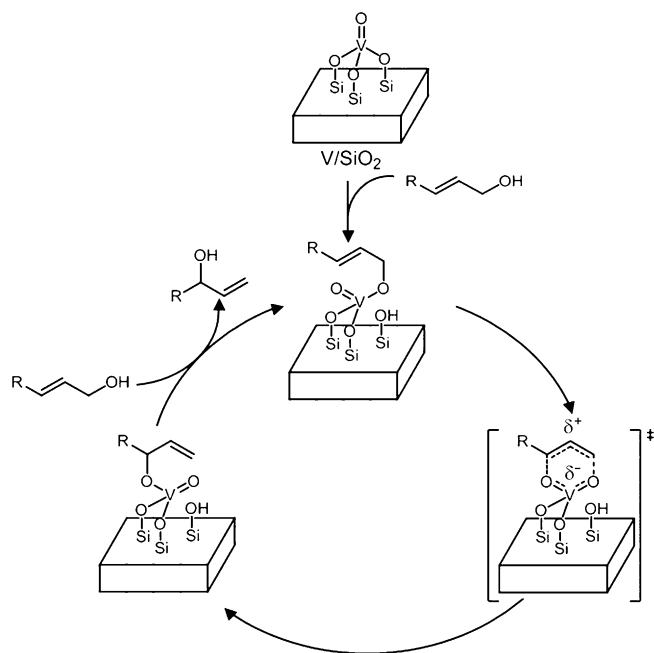


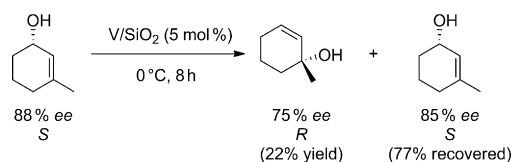
Figure 1. Plots of the yield of **2** and the fraction of monomeric V species as a function of V loading; the amounts of V used for the comparison of the catalytic activities of V/SiO₂ was constant (5 mol%). [a] The fraction of monomeric V species was calculated from the peak-area ratios in the UV/Vis absorption spectra (see the Supporting Information, Figure S2) according to the formula: Fraction of monomeric V species = (sum of the areas of the peaks at 250 and 300 nm/sum of the areas of peaks at 250, 300, 350, and 425 nm) × 100.^[27]

Figure 1. These results reveal that the formation of isolated mono-oxo V species on the SiO₂ support is essential for the efficient catalytic isomerization of allylic alcohols.

A proposed reaction mechanism for the 1,3-isomerization of an allylic alcohol in the presence of mono-oxo vanadium active species on SiO₂ is shown in Scheme 2: In the initial step, a vanadium species on the V/SiO₂ catalyst undergoes the exchange of one of its siloxy ligands with the allylic alcohol, thus forming a six-membered cyclic transition state.^[28] Subsequently, a migration of the allyl group onto a vanadium-oxo unit takes place, followed by further ligand exchange to regenerate the vanadium-alcoholate species with the formation of the isomerized product. This proposed reaction mechanism is strong-



Scheme 2. Proposed catalytic cycle for the V/SiO₂-catalyzed 1,3-isomerization of an allylic alcohol.



Scheme 3. 1,3-Isomerization of (*S*)-3-methyl-2-cyclohexen-1-ol by using V/SiO₂.

ly supported by the results of asymmetric 1,3-isomerization with V/SiO₂, as shown in Scheme 3. The treatment of (*S*)-3-methyl-2-cyclohexen-1-ol (88% ee) with V/SiO₂ gave the isomerized product (*R*)-1-methyl-2-cyclohexen-1-ol (75% ee), along with the starting material, with no significant change in its enantiomeric excess (85% ee). This phenomenon suggests that the isomerization of the hydroxy group occurs exclusively on one side of the C=C bond and, thus, that it does not involve the formation of an allylic cation intermediate.^[12]

In summary, silica-supported isolated vanadium oxide (V/SiO₂) represents a highly active heterogeneous catalyst for the 1,3-isomerization of various allylic alcohols under mild reaction conditions. The V/SiO₂ catalyst has a number of advantages: It is easily prepared, handled, and is applicable to preparative-scale reactions under solvent-free conditions. Moreover, the solid V/SiO₂ catalyst was separable from the reaction mixture and reusable without any degradation of its efficiency. The uniquely effective catalysis of V/SiO₂, which is outstanding among other supported-vanadium catalysts, may be attributed to the formation of isolated vanadium mono-oxo active species on the SiO₂ surface.

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Keywords: allylic compounds · heterogeneous catalysis · isomerization · supported catalysts · vanadium

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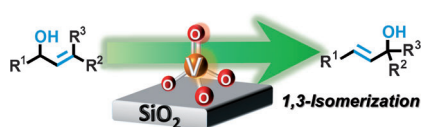
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Promotion by group high five: Silica-supported monomeric vanadium-oxide promoted the isomerization of various allylic alcohols, including under scaled-up and solvent-free reaction conditions. This catalyst also exhibited high reusability with no drop in activity.



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