133.2, 130.4, 127.6, 70.4, 61.7, 30.7, 27.8, 23.2, 21.7; HR-MS (MALDI-FTMS): *m*/*z* [M^++1] found: 337.0484, calcd for $C_{15}H_{18}O_3N_2SCl_2$: 337.0488.

5: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.4$ Hz, 2H), 7.26–7.18 (m, 6H), 6.88 (d, $J = 8.4$ Hz, 2H), 5.21 (d, $J = 4.4$ Hz, 1H), 4.56 (d, $J = 4.4$ Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.7$, 156.6, 145.7, 139.2, 133.8, 130.1, 128.8, 128.0, 127.7, 125.8, 72.0, 69.2, 61.4, 53.1, 21.6; HR-MS (MALDI-FTMS): *m*/*z* [M^++1] found: 441.0446, calcd for $C_{19}H_{18}O_4N_2SCl_2$: 441.0437.

6: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.4$ Hz, 2H), 7.26–7.19 (m, 6H), 6.90 (d, $J = 8.4$ Hz, 2H), 5.20 (d, $J = 4.3$ Hz, 1H), 4.55 (d, $J = 4.3$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.42 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.3$, 156.6, 145.7, 139.3, 133.9, 130.0, 128.8, 128.0, 127.7, 125.8, 72.1, 69.3, 62.3, 61.5, 21.6, 14.0; HR-MS (MALDI-FTMS): *m*/*z* [M^++1] found: 455.0587, calcd for $C_{20}H_{20}O_4N_2SCl_2$: 455.0594.

7: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (dd, $J = 1.8$, 6.6 Hz, 2H), 7.27–7.24 (m, 2H), 7.18 (s, 1H), 6.90 (d, $J = 8.2$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 5.17 (d, $J = 4.4$ Hz, 1H), 4.54 (d, $J = 4.4$ Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.8$, 156.4, 145.7, 137.9, 136.3, 133.9, 130.0, 129.4, 127.7, 125.7, 71.9, 69.2, 61.4, 53.1, 21.6, 21.1; HR-MS (MALDI-FTMS): *m*/*z* [M^++1] found: 455.0597, calcd for $C_{20}H_{20}O_4N_2SCl_2$: 455.0594.

8: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.83$ (dd, $J = 1.9$, 6.6 Hz, 2H), 7.38 (dd, $J = 1.9$, 6.6 Hz, 2H), 7.05 (s, 1H), 4.33 (s, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 1.26 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.5$, 153.3, 145.6, 134.3, 130.0, 127.8, 70.9, 69.5, 61.4, 52.3, 29.3, 23.1, 21.7; HR-MS (MALDI-FTMS): *m*/*z* [M^++1] found: 393.0437, calcd for $C_{15}H_{18}O_4N_2SCl_2$: 393.0449.

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[12] The common quenching treatment with aqueous Na_2SO_3 for *N*,*N*-dichlorosulfonamide-based reactions was not used to avoid some unknown side products. The loading of triphenylphosphane and the rhodium(II) heptafluorobutyrate dimer at 4.0 and 2.0 mol%, respectively, turned out to be near the turnover point since the reaction was not further accelerated in the presence of larger amounts of the catalyst. On the other hand, both the reaction rate and yield were diminished when a reduced amount of catalyst was used. Attempts to further optimize the reaction conditions were also made by using a variety of cosolvents of MeCN with other solvents, such as $CHCl_3$, CH_2Cl_2, toluene, and THF, in different ratios, but success was limited. An excess amount of $TsNCl_2$ (2.2 equiv) proved to be necessary for the complete consumption of the olefin starting materials. With the combination of rhodium/phosphane/4-Å MS in hand, we then went back to examine the combination of triphenylphosphane with the original rhodium compounds ($[Rh(OAc)_2]_2$ and $[Rh(OOCCF_3)_2]_2$), but failed to achieve any improvements. Surprisingly, when the triphenylphosphane ligand was replaced by tributylphosphane, only a tiny amount of the expected imidazolidine product was afforded, as revealed by crude ^1H NMR analysis.

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Efficient, Catalytic, Aerobic Oxidation of Alcohols with Octahedral Molecular Sieves**

Young-Chan Son, Vinit D. Makwana, Amy R. Howell, and Steven L. Suib*

The oxidation of alcohols to carbonyl compounds is of great interest to the fine chemicals industry and academia. Recently, catalytic oxidations of alcohols in which oxygen is the secondary oxidant have been the focus in many laboratories.[1–6] Alcohol oxidations using Ru,[2] Co,[3] Cu,[4] Pd,[5] and Pt[6] metal catalysts with additives, such as potassium carbonate, sodium bicarbonate, pyridine, molecular sieves, and phenanthroline, have been reported.

Stoichiometric metal oxidants such as chromates and active manganese dioxide have also been widely used.[7] In fact, conventional active manganese oxide has been most commonly used for allylic and benzylic oxidations. The reactivity of active manganese oxide is dependent on preparation methods, compositions, and structure.[7b, 8] Complicated preparation methods are often necessary, and the use of freshly made active manganese oxide is required. Moreover, five to fifty equivalents of this reagent are required to obtain oxidation products, which results in large amounts of nonreusable, toxic waste.

The problems associated with active manganese oxides prompted us to examine octahedral molecular sieves (OMS) as potential catalysts for alcohol oxidations. OMS materials

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are inexpensive, easy to make, and have received a great deal of attention because of their catalytic properties.[9] The K^+ ion form of hollandite (known as cryptomelane) is a microporous manganese oxide with a composition of $KMn_8O_{16} \cdot n\,H_2O$.[10] Synthetic cryptomelane octahedral molecular sieves (OMS-2) consist of structural units of MnO_6 octahedra, which are edge and corner shared. The structure of these materials contains 4.6×4.6 Å tunnels as a result of the 2×2 arrangement of octahedra; potassium ions are present in the tunnels with a small amount of water (Figure 1). The average manganese oxidation state of 3.8 of K-OMS-2 arises from the presence of a mixture of Mn^{4+}, Mn^{3+}, and Mn^{2+} ions.[10] This mixed valency of K-OMS-2, along with its one-dimensional tunnel structure, can give rise to interesting oxidation properties.[11] Pore size distribution studies show that a broad range of micropores are present, with diameters ranging from ~4.5 to 7 Å.[12] Herein, we report an evaluation of these materials as inexpensive, efficient, environmentally friendly, selective, aerobic, and heterogeneous catalysts, which do not require any additional co-oxidants for the oxidation of alcohols into carbonyl compounds. K-OMS-2 gave excellent conversions and 100% selectivities for benzylic alcohols without any additives (Table 1, Entries 1–3). However, K-OMS-2 did not provide a high conversion for relatively large substrates (Entry 4) or for allylic alcohols (Entries 5–8). Adding doping materials, such as Cr^{3+}, Ni^{2+}, and Co^{2+} ions, into the K-OMS-2 or using bases as additives decreased conversion.

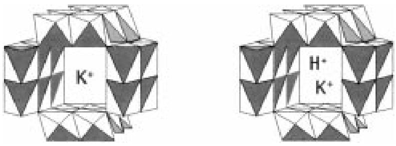
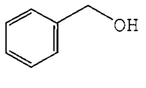
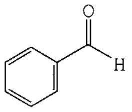
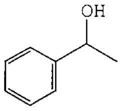
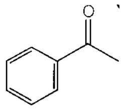
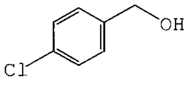
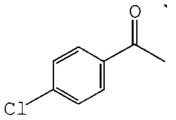
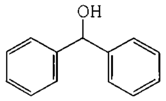
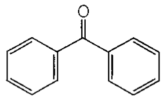
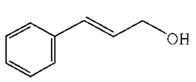
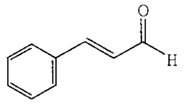
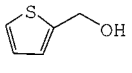
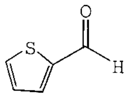
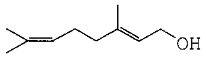
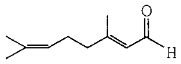
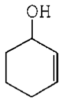
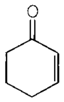
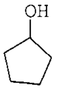
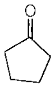
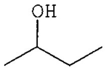
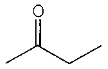


Figure 1. Structures of K-OMS-2 and H-K-OMS-2.

The use of H-K-OMS-2 (Figure 1) significantly enhanced conversion (Table 1). This result suggests that alcohol oxidations catalyzed by OMS-2 are accelerated by Brønsted acids. Benzylic (Entries 1–4) and allylic alcohols (Entries 5–8) undergo oxidation into the corresponding ketones and aldehydes with H-K-OMS-2. The catalyst is selective, even with sulfur heterocycles (Entry 6), geraniol gave geranial without any isomerization (Entry 7). For alkyl alcohols, the conversion was lower (Entry 9), and a greater amount of H-K-OMS-2 is required.

The reaction is also effective on a 20-mmol scale with no change in the conversion or reactivity. In addition, these OMS-2 materials are very stable and can be stored for a long time (activity retained after two years). Over oxidation did not occur with K-OMS-2 or H-K-OMS-2. Air can be used instead of more expensive oxygen, although oxygen shortens the reaction time and increases conversion.[13] When nitrogen was used instead of air, the conversion significantly decreased to 10%. This is because the catalyst is used without pretreatment and there is a significant amount of adsorbed oxygen on the surface.

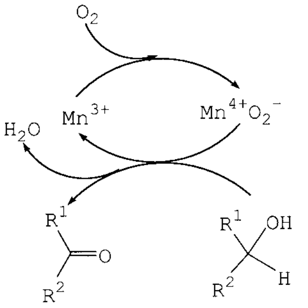
Table 1. The oxidation of various alcohols catalyzed by OMS-2 in the presence of air.[a,b]

Entry	Substrate	Product	Catalyst	Conversion [%][c]
1			K-OMS-2 H-K-OMS-2	90(85)[d] 97(93)[d]
2			K-OMS-2 H-K-OMS-2	93 99
3			K-OMS-2 H-K-OMS-2	95 99
4			K-OMS-2 H-K-OMS-2	35 100
5			K-OMS-2 H-K-OMS-2	50 95
6			K-OMS-2 H-K-OMS-2	40 100
7			K-OMS-2 H-K-OMS-2	5 95
8			K-OMS-2 H-K-OMS-2	30 90
9			K-OMS-2 H-K-OMS-2	35[e] 67[e]
10			H-K-OMS-2	35[f]

[a] Reactions were performed at 110 °C, under toluene reflux and air for 4 h. [b] The selectivity of all oxidation reactions is 100%. [c] The conversion was measured by gas chromatography and ^1H NMR spectroscopy using internal standard methods. [d] Yield of isolated product. [e] The reaction time was 20 h. [f] The reaction time was 16 h.

After the oxidation reaction, filtered H-K-OMS-2 was washed with methanol and water and heated to 300 °C and could then be reused as a catalyst without any appreciable loss of activity for oxidation. Water, which is the only side product produced from the oxidation reaction, poisons the catalyst. The catalyst can also physically absorb the aldehydes formed in the reaction. X-ray diffraction (XRD) and infrared (IR) spectroscopy studies indicated that after being heated to 300 °C the catalyst returned to its original composition and structure. Temperature-programmed desorption studies of used catalysts show only desorption of H_2O, reactant, or product. The standard Mn leaching experiment[14] was performed to ascertain if the reaction is truly heterogeneous: Conversion did not change after filtering off the catalyst at reaction temperature and letting the reaction continue. This result demonstrates that the reaction is heterogeneous. Any manganese that leached into solution is not an active homogeneous catalyst. A minimum turnover number based on total moles of manganese and H^+ ions, is approximately 80. A minimum turnover number based on total moles of H^+ ions is 400. The surface area of OMS-2 was varied from 20–250 $m^2 g^{-1}$, and no correlation of activity and surface area was observed (no change in rates). In fact, K-OMS-2 with a larger surface area (97 $m^2 g^{-1}$) was less active than H-K-OMS-2, which has a smaller surface area of 85 $m^2 g^{-1}$. The pore size distributions of K-OMS-2 and H-K-OMS-2 are the same.

The active sites of OMS-2 may be derived from Mn^{3+} ions in tunnel sites in the OMS-2 materials. This can be inferred from the lower reactivity towards large substrates such as 1-acenaphthenol (conversion of $<5\%$ after 24 h). A redox mechanism is considered to involve alcohol oxidation by $Mn^{4+}O_2^-$, which is reduced to Mn^{3+} ions only to be reoxidized by dioxgen (Scheme 1). The formation of dioxygen–manganese complexes may be considered to produce activated oxygen.



Scheme 1. Proposed outline of the mechanism of alcohol oxidation with OMS-2. $R^1 = R^2$; $R^1 \neq R^2$; full list of substrates shown in Table 1.

Mechanistic studies such as kinetic modeling and ^{18}O labeling experiments point to a Mars–van Krevelen mechanism of oxidation rather than the Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate law of heterogeneous catalysis. The Mars–van Krevelen mechanism can be described by Equations (1) and (2) where M=O is the oxidized catalyst, S is an organic substrate, and M is the reduced catalyst. According to this mechanism, lattice oxygen of OMS-2 participates in the oxidation reaction and is later replenished by fluid-phase oxygen. The active species is presumably the O_2^- ion, this indicates a simultaneous transfer of two electrons and not a stepwise electron donation.

$$M{=}O + S \longrightarrow M + S{=}O \qquad (1)$$

$$2\,M + O_2 \longrightarrow 2\,M{=}O \qquad (2)$$

In conclusion, to our knowledge, this is the first example of acid-catalyzed alcohol oxidations with inexpensive, crystalline manganese oxides as catalysts. Octahedral molecular sieves (K-OMS-2 and H-K-OMS-2) without the use of additives catalyzed the oxidation of alcohols to the corresponding aldehydes and ketones under mild conditions. H-K-OMS-2 gave excellent conversions and very high selectivity in the oxidation of alcohols. H-K-OMS-2 is an efficient, selective, easily regenerable and environmentally friendly catalyst. H-K-OMS-2 is inexpensive to make and requires no co-oxidants.

Experimental Section

Preparation of synthetic cryptomelane (OMS-2):[10] Potassium permanganate solution (225 mL, 0.4 M) was added to a 500 mL round-bottomed flask containing a mixture of manganese sulfate hydrate solution (67.5 mL, 1.75 M) and concentrated nitric acid (6.8 mL). The dark brown slurry was heated under reflux for 24 h, then filtered and washed with deionized water several times. The catalyst was dried at 120 °C overnight before use.

H-K-OMS-2: K-OMS-2 was stirred in a 1 M solution of nitric acid for several hours at 60–70 °C, forming H-K-OMS-2. After the washing and drying procedure outlined above, the catalyst was ready for use. Elemental analysis showed that H-K-OMS-2 has the formula $H_{0.2}K_{0.8}Mn_8O_{16} \cdot n\,H_2O$.

A typical procedure for the alcohol oxidation: Toluene (10 mL) and the alcohol (1 mmol) were first added to a round-bottomed flask containing K-OMS-2 (0.05 g; ~0.5 equiv, one manganese was considered to be one active site), represented by $KMn_8O_{16} \cdot n\,H_2O$ ($n = 0.5-10$). The mixture was then stirred under reflux (110 °C) in air. After 4 h, the reaction mixture was cooled, K-OMS-2 was removed by filtration, and the filtrate was analyzed using gas chromatography/mass spectrometry (GC/MS), ^1H NMR, and IR spectroscopy.

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1-Silyl-1-boryl-2-alkenes: Reagents for Stereodivergent Allylation Leading to 4-Oxy-(*E*)-1-alkenylboronates and 4-Oxy-(*Z*)-1-alkenylsilanes[**]

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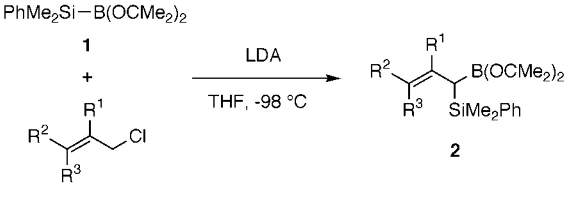
Takuya Kurahashi, and Tamejiro Hiyama*

Allylmetal reagents have been widely used in organic synthesis.[1] In addition, allylic boranes[2] and silanes[3] are highly versatile owing to their wide availability, high stability, and low toxicity as well as excellent chemo-, regio-, and stereoselectivities. In sharp contrast, little attention has been paid to 1-silyl-1-boryl-2-alkenes, though such reagents can be regarded as a hybrid of allylic boranes and silanes and are attractive for the construction of stereochemically complex molecules.[4] Yamamoto, Yatagai, and Maruyama prepared α-trimethylsilyl-substituted crotyl-9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane) by deprotonation of crotyl-9-BBN followed by silylation with chlorotrimethylsilane.[5] Similar boronates were synthesized by Tsai and Matteson by the homologation of alkenylboronates with [chloro(trimethylsilyl)methyl]lithium.[6] Both reagents were found to allylate aldehydes[7] in a manner similar to allylic boranes. Although this methodology is effective for acyclic stereocontrol, allylation with allylic silanes and stereospecificity in boron-selective allylation remained to be explored. Herein we describe the novel stereocontrolled synthesis of 1-silyl-1-boryl-2-alkenes by *gem*-silylborylation of α-chloroallyllithiums and dual stereospecific allylation of aldehydes with silicon or boron functionality of the *gem*-silylboryl reagents.

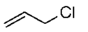
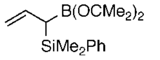
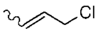
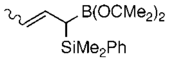
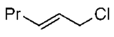
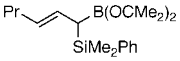
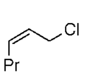
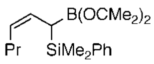
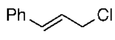
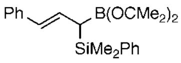
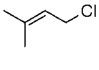
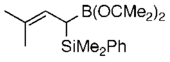
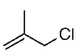
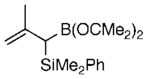
Recently, the novel *gem*-silylborylation reaction of 1-halo-1-lithio-1-alkenes with (dimethylphenylsilyl)(pinacolato)borane (**1**) was disclosed[8] and is considered to proceed via borate formation followed by 1,2-migration of a silyl group from an ate-type boron to a carbenoid carbon. We envisaged that the title *gem*-silylboryl reagents **2** might be prepared readily by the *gem*-silylborylation with **1** of vinyl-substituted carbenoids [Eq. (1)].[9, 10] Thus, we treated **1**[11] with α-chloroallyllithiums



(1)

generated in situ from allylic chlorides and lithium diisopropylamide (LDA) in THF at −98 °C. The results are summarized in Table 1. Allyl chloride was converted into **2a** in 82% yield (Entry 1). Substituted allylic chlorides were also *gem*-silylborylated smoothly in good yields irrespective of the substitution pattern (Entries 2–7). No trace of γ-silyl-α-boration by 1,4-migration of a silyl group was observed. Noteworthy is that the olefinic configuration was perfectly retained in compounds **2** (Entries 3–5): stereochemically pure allylic chlorides gave single stereoisomers of **2**.

Table 1. Synthesis of 1-silyl-1-boryl-2-alkenes from allylic chlorides.[a]

Entry	Allylic chloride	Product	Yield [%][b]
1		 **2a**	82
2	 [c]	 **2b**	86[d]
3	 [e]	 **2c**	75[e]
4	 [f]	 **2d**	79[f]
5	 [e]	 **2e**	75[e]
6		 **2f**	72
7		 **2g**	73

[a] allylic chloride (1.0 mol), **1** (1.1 mol), LDA (1.0 mol), THF, −98 °C, 10 min then warmed to room temperature. [b] Isolated yields are given. [c] *E*/*Z* = 85:15. [d] *E*/*Z* = 83:17. [e] *E*/*Z* = >99:<1. [f] *E*/*Z* = <1:>99.

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