Supported Catalysts

Heterotrimetallic RuMnMn Species on a Hydrotalcite Surface as Highly Efficient Heterogeneous Catalysts for Liquid-Phase Oxidation of Alcohols with Molecular Oxygen**

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The creation of a well-defined, active metal site on a solid surface not only opens up an avenue to materials that boost catalytic performance but also aids an understanding of the molecular basis of heterogeneous catalysis.[1] Modifying the coordination sphere of a metal species with other metals as ligands, which is a basic approach in organometallic and bioinorganic chemistry,[2] is also being applied to heterogeneous catalysis[3] because of the potential of performing unique catalytic reactions based on cooperation between diverse metals within a regular arrangement. In addition, this allows local compositional modeling for the strong metal–support interactions (SMSI) seen in supported metal catalysts.[4]

Hydrotalcite (HT), which is a layered, mixed hydroxide of Mg and Al,[5] has received attention as a material for advanced heterogeneous catalysts[6,7] because of the cation-exchange ability of the Brucite layer, the anion-exchange ability of the interlayer, its adjustable surface basicity, and adsorption capacity. Recently, we created a monomeric Ru^{IV}-OH species on the HT (Ru/HT) surface by adsorption which turned out to be an excellent heterogeneous catalyst for the one-pot synthesis of α-alkylated nitriles by a Ru-catalyzed alcohol oxidation coupled with a base-promoted aldol reaction.[7d] As part of our ongoing project on the functionalization of supported Ru catalysts to achieve environmentally friendly ("green") organic syntheses, we present a novel HT-bound heterotrimetallic $Ru^{IV}Mn^{IV}Mn^{IV}$ species that has been structurally characterized on the atomic scale by X-ray absorption spectroscopy.[8] This material is an excellent solid catalyst for liquid-phase alcohol oxidation under mild conditions. This protocol to create a supported mixed-metal species can provide catalytically active compounds that are uniform in composition and distribution on a solid surface by applying concepts from coordination chemistry, and bridges the gap between homogeneous and heterogeneous catalysis.[9]

We obtained well-defined, heterotrimetallic RuMnMn species on the HT surface ($RuMn_2$/HT) by immobilizing Mn cations onto Ru/HT. The Ru/HT was prepared by treating HT with an aqueous solution of $RuCl_3 \cdot n H_2O$.[7d] The retention of the HT interlayer distance (3.0 Å), as shown by XRD (X-ray diffraction),[10] indicated that both metal species are accommodated on the HT surface. The K-edge XANES (X-ray absorption near-edge structure) spectrum of the Ru and Mn of $RuMn_2$/HT reveals that the surface Ru and Mn cations are in the oxidation state +IV. In the Fourier transformation of the Ru K-edge k^3-weighted EXAFS (extended X-ray absorption fine structure) spectrum of $RuMn_2$/HT (Figure 1b) a peak near 3.5 Å, corresponding to the contiguous Ru sites (Ru–O–Ru),[11] was barely detected.

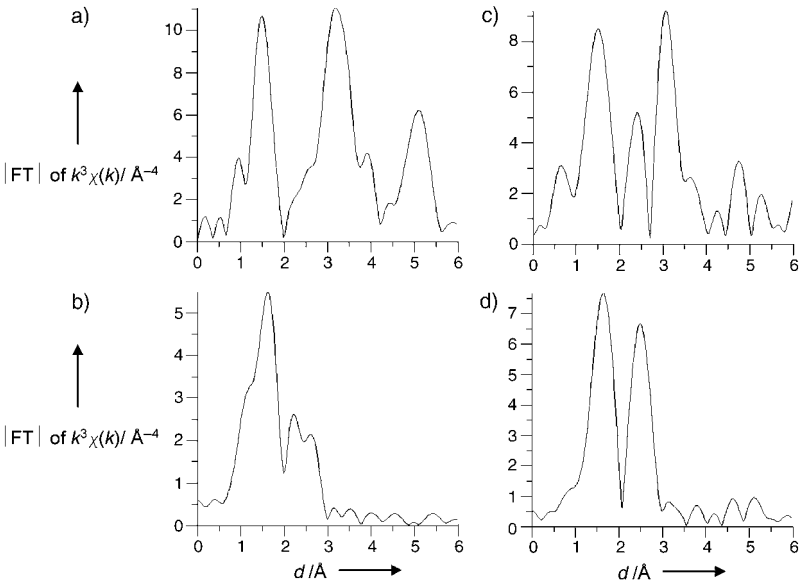

Figure 1. Fourier transformation (FT) of the k^3-weighted K-edge EXAFS spectrum of a) RuO_2, b) $RuMn_2$/HT (Ru K-edge), c) β-MnO_2, and d) $RuMn_2$/HT (Mn K-edge). The phase shift was not corrected.

The coordination number (CN), distance (R), and Debye–Waller factor (Δσ) of the Ru–O, Ru–Mg, and Ru–Mn bonds, as estimated by a curve-fitting analysis,[8] are listed in Table 1. The Ru^{IV} species of $RuMn_2$/HT are surrounded by six oxygen atoms with different bond distances. The shortest Ru–O bond was assigned to a Ru^{IV}–OH moiety.[12] Two bonds of Ru–Mg and Ru–Mn shells, with CNs of 0.9 and 1.9, respectively, prove that the Ru^{IV} species is in the vicinity of the Mg cation within the Brucite-like sheets and two Mn cations on the HT surface. Furthermore, a Mn–Mn shell with a distance of 2.32 Å and CN of 1.1 shows the formation of dimeric Mn^{IV} cation species.[13]

The above results show a $Ru^{IV}Mn^{IV}Mn^{IV}$ trimetallic species on the HT surface, as shown in Figure 2, in which dimeric Mn–Mn species are connected to a single Ru^{IV} cation through OH groups and water. To our knowledge, this is the first report of the preparation of heterotrimetallic species

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Table 1: Curve-fitting results for K-edge EXAFS of Ru and Mn.

Sample	Shell	CN[a]	*R* [Å][b]	Δσ [Å²][c]
$RuMn_2$/HT	Ru-K			
	Ru–O(1)	2.1	1.97	−0.0079
	Ru–O(2)	2.1	2.07	−0.0045
	Ru–O(3)	1.1	1.83	−0.0088
	Ru–O(4)	0.6	2.61	−0.0087
	Ru–Mg	0.9	3.19	−0.1023
	Ru–Mn	1.9	3.28	0.0499
	Mn-K			
	Mn–O(1)	2.6	1.85	−0.0030
	Mn–O(2)	3.1	1.98	−0.0060
	Mn–Mn	1.1	2.32	−0.0017
RuO_2[d]	Ru–O(1)	2	1.94	–
	Ru–O(2)	4	1.98	–
β-MnO_2[e]	Mn–O	6	1.89	–
	Mn–Mn(1)	2	2.87	–
	Mn–Mn(2)	8	3.42	–

[a] Coordination number. [b] Interatomic distance. [c] Δσ is the difference between the Debye–Waller factor of the sample and that of the reference sample. [d] Taken from the crystallographic data.[11] [e] Taken from the crystallographic data.[26]

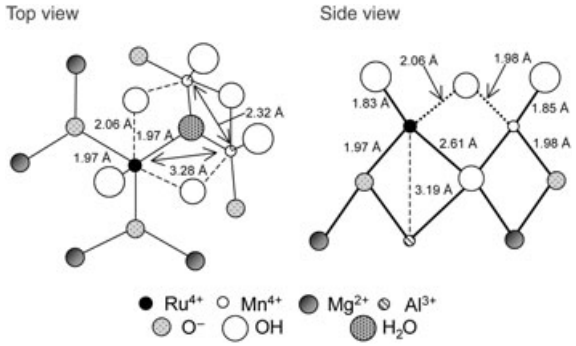


Figure 2. Proposed structure of the heterotrimetallic RuMnMn species on HT.

consisting of metal cations on a support involving metal oxide and metal hydroxides,[14] whereas the preparation of supported heterobimetallic or metal alloy species have been reported.[3] Adjusting the basicity of the hydroxy groups around the Ru^{IV} cation, produced by reaction of the surface OH groups of HT with $RuCl_3$ species,[7d] brought about selective immobilization of Mn cations in the vicinity of the Ru species to give the unique $Ru^{IV}Mn^{IV}Mn^{IV}$ sites.

The catalytic ability of the RuMnMn species was explored in the oxidation of alcohol with O_2 at atmospheric pressure (Table 2).[15,16] The trimetallic $RuMn_2$/HT shows a higher catalytic activity than Ru/HT,[7d] Ru/Al_2O_3,[15c,e] and RuO_2,[15a] which are typical heterogeneous Ru catalysts for the oxidation of benzyl alcohol (**1**).[17] Benzyl alcohol was oxidized to benzaldehyde (**2**) quantitatively within 1 h in the presence of the $RuMn_2$/HT catalyst.[18]

Table 2: Oxidation of benzyl alcohol (**1**) in the presence of various Ru catalysts under 1 atm O_2.[a]

Entry	Catalyst	Conv. [%][b]	Yield [%][b]
1	$RuMn_2$/HT	100	99
2	reuse 1[c]	100	99
3	reuse 2[c]	100	98
4	reuse 3[c]	100	99
5	Ru/HT	66	66
6	Ru/Al_2O_3[d]	56	55
7	$RuO_2 \cdot n H_2O$	5	4
8	Mn_2/HT[e]	0	0
9	HT	0	0

[a] Reaction conditions: catalyst (3 mol% Ru), benzyl alcohol (1 mmol), toluene (5 mL), 60°C, 1 atm O_2, 1 h. [b] Conversions and yields were determined by GC analysis using an internal standard method based on benzyl alcohol. [c] Catalyst recovered and reused. [d] Prepared by the reported procedure.[15c] [e] 6 mol% Mn.

The initial turnover frequency based on Ru for $RuMn_2$/HT (140 h^{-1}) is almost five times larger than that for Ru/HT. On a 10-mmol scale oxidation of **1** in the presence of 0.1 mol% Ru, the turnover number based on Ru reached 840 at 90°C. Moreover, the high catalytic ability of $RuMn_2$/HT was demonstrated by the quantitative oxidation of **1** within 10 h, even at 40°C.

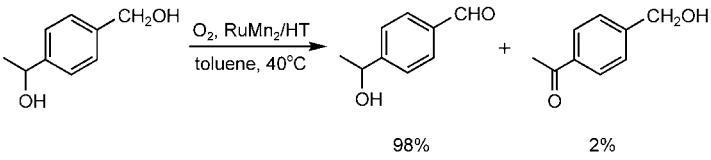
As displayed in Table 3, the $RuMn_2$/HT catalyst selectively oxidizes a wide variety of alcohols. Primary and secondary benzylic alcohols are converted into the corresponding carbonyl compounds in high yield (entries 1–3). The catalysis is also chemoselective; $RuMn_2$/HT preferentially oxidizes primary over secondary hydroxy groups, as shown by the selective oxidation of 1-[(4′-hydroxymethyl)phenyl]ethanol to 1-[(4′-formyl)phenyl]ethanol in 98% yield (Scheme 1).

In the case of cyclopropyl(phenyl)methanol, the hydroxy group was oxidized without cleavage of the cyclopropyl ring

Table 3: Oxidation of various alcohols catalyzed by $RuMn_2$/HT in the presence of O_2.[a]

Entry	Alcohol	Product	*t* [h]	Conv. [%]	Yield [%][b]
1	Benzyl alcohol (**1**)	Benzaldehyde (**2**)	1	100	99
2	1-Phenylethanol	Acetophenone	3.5	100	92
3	Benzhydrol	Benzophenone	2	94	93
4	Cyclopropyl(phenyl)methanol	Cyclopropyl phenyl ketone	6	100	99
5	Cinnamyl alcohol	Cinnamaldehyde	1.5	100	97
6	(2-Hydroxymethyl)thiophene	2-Thiophenecarboxaldehyde	2	100	89
7	2-Aminobenzyl alcohol	2-Aminobenzaldehyde	21	100	100

[a] Reaction conditions: catalyst (2 mol% Ru), alcohol (1 mmol), toluene (5 mL), 60°C, O_2 flow. [b] Yields were calculated based on alcohols.



Scheme 1. Selective oxidation of primary hydroxy groups by $RuMn_2$/HT catalyst.

(entry 4). Oxidation of cinnamyl alcohol proceeded smoothly without affecting the carbon–carbon double bond (entry 5). Furthermore, $RuMn_2$/HT effectively catalyzes the oxidation of (2-hydroxymethyl)thiophene, a heteroaromatic alcohol, to 2-thiophenecarboxaldehyde, in high yield (entry 6), and the oxidation of 2-aminobenzyl alcohol to 2-aminobenzaldehyde, quantitatively (entry 7), in contrast to the homogeneous Pd and Ru complexes.[16]

The spent $RuMn_2$/HT catalyst could be readily separated from the reaction mixture by filtration. The EXAFS spectrum of the recovered $RuMn_2$/HT catalyst confirmed retention of the original RuMnMn structure, and ICP (inductively coupled plasma) analysis of the filtrate indicated no leaching of Ru and Mn species during the oxidation. The $RuMn_2$/HT catalyst could be reused while maintaining the same high catalytic activity and selectivity (Table 2, entries 2–4). When the catalyst was removed at about 50% conversion of the alcohol, no further oxidation was detected in the filtrate after 3 h under 1 atm O_2 which shows that the present alcohol oxidations proceed at the interface between the catalyst surface and the liquid phase.

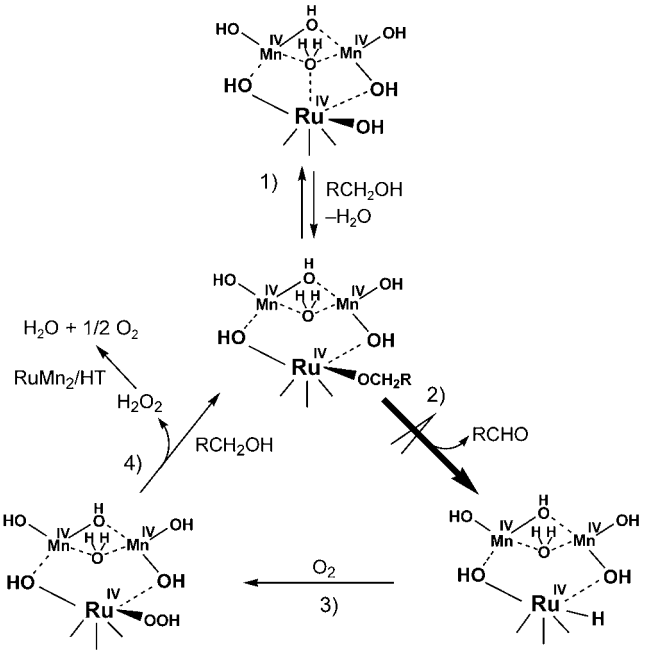
To the best of our knowledge, $RuMn_2$/HT is the most effective, environmentally benign Ru catalyst for the oxidation of benzylic and aromatic allylic alcohols in the liquid phase[15,16c,d,19] with the advantages of 1) high catalytic activity, even with O_2 at 1 atm as the sole oxidant, 2) wide applicability to alcohols, including those containing heteroatoms, 3) simple preparation and work-up procedures, and 4) reusability as a solid catalyst.

The Mn cations in the RuMnMn species evidently play a pivotal role in improving the Ru-catalyzed alcohol oxidation since Mn_2/HT does not catalyze the reaction (Table 2, entry 8). We have proposed a catalytic cycle for the alcohol oxidation (Scheme 2)[20] that proceeds via a ruthenium alkoxide intermediate, which undergoes β-hydrogen elimination to produce the carbonyl compound and a ruthenium hydride species, as observed by IR spectroscopy.[10] Reaction of this hydride with O_2 and subsequent ligand-exchange with the alcohol completes the catalytic cycle.[15b,c]

A rate equation based on a Michaelis–Menten-type model[21] for this proposed mechanism [Eq. (1)] agrees well with the kinetic data.

$$\mathrm{Ru{-}OH + RCH_2OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{[Ru{-}OCH_2R]} \xrightarrow{k_2} \mathrm{Ru{-}H + RCHO} \qquad (1)$$

For the $RuMn_2$/HT-catalyzed oxidation of **1**, K_M and k_2 were calculated to be 2.96 mM and 0.047 s^{-1}, respectively, at 60 °C. The rate constant (k_2) of β-hydrogen elimination from the ruthenium alkoxide intermediate is therefore almost twice that for the Mn-free Ru/HT. The β-hydrogen elimination is considered as the rate-determining step in the overall alcohol oxidation from the primary kinetic isotope effect in the competitive oxidation of **1** and $C_6D_5CD_2OH$ (4.2).[15b,e] Thus, the Mn cations in the heterotrimetallic sites facilitate β-hydrogen elimination from the ruthenium alkoxide intermediate. Removing the water molecule that binds the Ru and Mn cations improves the situation of the Ru species during β-hydrogen elimination by, for example, producing a coordinately unsaturated Ru site.[16c]



Scheme 2. A proposed mechanism for the oxidation of a primary alcohol by trimetallic RuMnMn sites.

For the secondary alcohol 1-phenylethanol, K_M and k_2 were found to be 133 mM and 0.026 s^{-1}, respectively, at 60 °C. Importantly, the K_M value is significantly greater than that for the oxidation of **1**, which is reflected in the preferential oxidation of primary hydroxy groups by this species.[22] The formation of metal alkoxide intermediates of primary alcohols is favored over secondary alcohols in the ligand-exchange step.[23]

In summary, a robust heterotrimetallic $Ru^{IV}Mn^{IV}Mn^{IV}$ species coordinated to a hydrotalcite surface as a macroligand facilitates the highly efficient aerobic oxidation of alcohols. Such cooperative action among high-valence metal cations in a heterometallic species on a solid surface provides a unique protocol for the preparation of functionalized heterogeneous catalysts for environmentally benign organic syntheses.[24] Ongoing efforts are focused on creating high-valence Ru cation species, that is, Ru^{VI} and Ru^{VII}, based on the redox interaction within a heterometallic site for highly efficient epoxidation and dihydroxylation reactions of alkenes with molecular oxygen.

Experimental Section

Ru/HT[7d] was treated with an aqueous solution of $MnCl_2{\cdot}4H_2O$ to afford $RuMn_2$/HT.[10] Elemental analysis (%) calcd for $Ru_{0.071}Mn_{0.142}/Mg_6Al_2(OH)_{16}CO_3$: Ru 1.03, Mn 1.12, Mg 21.0, Al, 8.14; found: Ru 1.05, Mn 1.20, Mg 21.4, Al 7.9.

The X-ray absorption spectra were recorded at the BL01B1 beamline in SPring-8 of JASRI, Japan (2003B0944-UXa-np and 2004A489-NXa-np) and at the BL-10B beamline of PF at KEK, Japan (2001G143 and 2002G102). The data were reduced using computer

systems at the Data Processing Center of Kyoto University according to a previously reported procedure.[25]

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[17] See the Supporting Information for typical time courses for the oxidation of **1**.

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