Ruthenium-Immobilized Periodic Mesoporous Organosilica: Synthesis, Characterization, and Catalytic Application for Selective Oxidation of Alkanes

Nobuhiro Ishito,[a,b,d] Hirokazu Kobayashi,[a,b] Kiyotaka Nakajima,[a,b] Yoshifumi Maegawa,[c,d] Shinji Inagaki,[c,d] Kenji Hara,*[a,d,e], and Atsushi Fukuoka*[a,b]

Dedication ((optional))

Abstract: Periodic mesoporous organosilica (PMO) is a unique material that has a crystal-like wall structure with coordination sites for metal complexes. A Ru complex, $[RuCl_2(CO)_3]_2$, is successfully immobilized onto 2,2'-bipyridine (BPy) units of PMO to form a single site catalyst, which has been confirmed by various physicochemical analyses. Using NaClO as an oxidant, the Ru-immobilized PMO oxidizes the tertiary C−H bonds of adamantane to the corresponding alcohols at 57 times faster than the secondary C−H bonds, thereby exhibiting remarkably high regioselectivity. Moreover, the catalyst converts *cis*-decalin to *cis*-9-decalol in 63% yield with complete retention of the substrate stereochemistry. The Ru catalyst can be separated by simple filtration and reused without loss of the original activity and selectivity for the oxidation reactions.

Introduction

Periodic mesoporous organosilicas (PMOs) are unique materials that possess uniform mesopores (2-30 nm) that consist of crystal-like ordered arrays of organic moieties bridged by siloxane bonds.[1,2] Various chemical and physical properties can be introduced into the PMO materials by varying the organic groups. Ethylene-bridged PMO provides a highly hydrophobic environment inside the restricted mesopores that can stabilize protein molecules.[3] A coumarin-doped biphenyl-PMO system exhibits unique UV light absorption and subsequent fluorescence by a light-harvesting effect; the photoexcitation of biphenyl moieties by UV light adsorption induces energy transfer to coumarin dye immobilized within mesopores, which results in highly efficient fluorescence.[4] A photocatalytic CO_2 reduction system was constructed by anchoring a Re complex onto biphenyl-incorporated PMO.[5] Recently, a PMO with incorporated 2,2'-bipyridyl (BPy) groups, BPy-PMO, was successfully synthesized and exhibited high performance as a solid chelating ligand for the immobilization of metal complexes to produce new types of single-site heterogeneous catalysts. An Ir-immobilized BPy-PMO catalyzed the borylation of C–H bonds in substituted benzenes to afford desired products.[6] and the activity of the solid catalyst was higher than that of a corresponding homogeneous catalyst. Immobilization of a Ru complex on BPy-PMO was also reported to be promising for solar energy conversion systems.[6] After loading Pt nanoparticles, the Ru-supported BPy-PMO continuously reduced protons in water into hydrogen in the presence of a sacrificial reagent (ethylenediaminetetraacetic acid; EDTA) under visible-light irradiation. Direct injection of photoexcited electrons from the Ru complex to Pt nanoparticles enabled efficient hydrogen production, even in the absence of a typical electron mediator such as methyl viologen.

We speculate that a prospective application of PMO-based catalysts is the partial oxidation of hydrocarbons, which is a significant challenge in catalysis.[7-10] The oxidation of hydrocarbons using metal complex catalysts is subject to oxidation of the ligands by their own active oxygen species.[11] To avoid this problem, oxidation enzymes, as typified by cytochrome P-450, rigidly fix the active center (iron protoporphyrin-IX) in an isolated state on the pore wall of a protein.[12] It is thus expected that the immobilization of isolated active sites directly on the pore walls of PMOs will suppress self-oxidation, which is in sharp contrast to conventional catalysts[13] with mobile active centers grafted through linkers.

Herein, we report a new and reusable Ru-immobilized BPy-PMO catalyst that achieves selective oxidation of alkanes. The catalyst was synthesized from $[RuCl_2(CO)_3]_2$ and BPy-PMO; various physicochemical analyses verified the formation of a uniform chemical structure with the Ru complex on PMO. The Ru catalyst oxidizes adamantane and *cis*-decalin to the corresponding tertiary alcohols with excellent regio- and stereoselectivity using a practical oxidant (NaClO). No solid catalyst has achieved high selectivity or durability in the oxidation of these alkanes. Although several homogeneous metal complexes have already shown high selectivity, these are

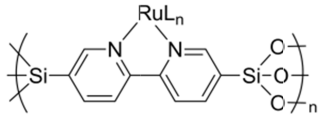
[a] N. Ishito, Dr. H. Kobayashi, Dr. K. Nakajima, Dr. K. Hara, Prof. Dr. A. Fukuoka
Catalysis Research Center
Hokkaido University
Sapporo, Hokkaido 001-0021 (Japan)
E-mail: Fukuoka@cat.hokudai.ac.jp
[b] N. Ishito, Dr. H. Kobayashi, Dr. K. Nakajima, Prof. Dr. A. Fukuoka
Graduate School of Chemical Sciences and Engineering
Hokkaido University
Sapporo, Hokkaido 060-8628 (Japan)
[c] Y. Maegawa, Dr. S. Inagaki
Toyota Central R&D Laboratories, Inc.
Nagakute, Aichi 480-1192 (Japan)
[d] N. Ishito, Y. Maegawa, Dr. S. Inagaki, Dr. K. Hara
Japan Science and Technology Agency (JST)/ACT-C
Nagakute, Aichi 480-1192 (Japan)
[e] Dr. K. Hara
School of Engineering
Tokyo University of Technology
Hachioji, Tokyo 192-0982 (Japan)

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

single-use catalysts.[10,14] In contrast, the immobilization of the Ru complex on BPy-PMO realizes both high selectivity and reusability for the oxidation of alkanes. Tertiary alcohols of adamantane are precursors to photoresists for ArF lithography, engineering plastics, and medicines.[15,16] The selective oxidation of decalin is a model reaction for the synthesis of steroids and terpene based anti-tumor medicines.[10,17] It is thus expected that the Ru-immobilized PMO catalyst developed in this study will contribute to practical industrial applications of fine chemical synthesis.

Results and Discussion

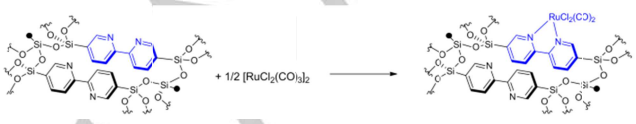
Characterization of 1: PMO-based catalyst **1** was synthesized using BPy-PMO and $[RuCl_2(CO)_3]_2$ (Scheme 1) and characterized in detail. Immobilization of Ru complexes on BPy-PMO was also conducted using other Ru precursors, $RuCl_3{\cdot}xH_2O$ and $RuCl_2(bpy)_2{\cdot}2H_2O$, to obtain the Ru-immobilized BPy-PMOs, denoted as **2** and **3**, respectively (Figure 1).



RuL_n = $RuCl_2(CO)_2$ (**1**), $RuCl_3$ (**2**), $RuCl_2(bpy)_2$ (**3**).

Figure 1. Plausible structures of **1**, **2** and **3**.

Nitrogen adsorption experiments of BPy-PMO and **1** both provided type-IV isotherms with no hysteresis, which indicates uniform mesopores (Figure 2a). Non-linear density functional theory (NLDFT) analysis of the isotherms indicated that the pore diameter decreases from 4.6 to 4.0 nm after Ru loading (Figure 2b). The Brunauer-Emmett-Teller (BET) specific surface area was also slightly decreased from 690 to 530 $m^2\ g^{-1}$ by impregnation of Ru complexes onto BPy-PMO. The amount of surface BPy units in BPy-PMO was estimated to be 2.2 mmol g^{-1}, which was obtained by dividing the BET surface area (690 $m^2\ g^{-1}$) by the cross-sectional area of a PMO unit (310 $m^2\ mmol^{-1}$ for Si-BPy-Si-O_3; Figure 1). XRD measurements of BPy-PMO and **1** represented similar diffraction lines at 2θ = 1.8° (100) (Figure S1). These results clearly show that the ordered mesoporous structure of BPy-PMO is preserved after formation of the Ru complex. Characterization data for the other Ru catalysts **2**, **3**, and **4** are summarized in Supporting Information (Figures S2, S3, S4).



Scheme 1. Synthesis of Ru-immobilized BPy-PMO.

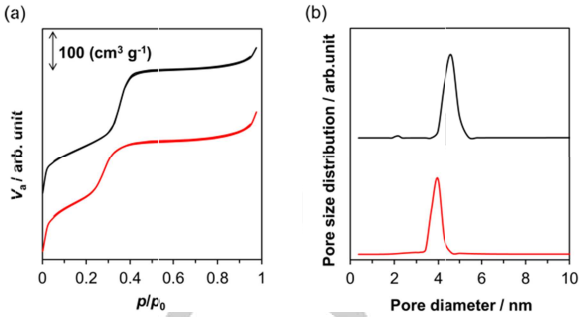


Figure 2. (a) N_2 adsorption isotherms and (b) NLDFT pore diameter distributions for BPy-PMO (black) and 1 (red) at 77 K.cheme 1. Synthesis of Ru-immobilized BPy-PMO.

EDX analysis indicated that the amount of Ru in **1** is 0.30 mmol g^{-1} (3.0 wt%), which corresponds to 15% of the total BPy units on the surface. This ratio of Ru/BPy is more than double the ratio previously reported for **3** (7.1%).[6] In a control experiment, it was verified that no Ru complex is immobilized on a mesoporous silica without BPy ligands.

Figure 3 shows UV-vis DRS spectra of BPy-PMO, **1**, the precursor $[RuCl_2(CO)_3]_2$, and $RuCl_2(bpy)(CO)_2$ as a model of **1**. BPy-PMO gave a broad peak at 300 nm derived from π–π* transition for BPy units within the silica framework.[19] A new peak was observed at 410 nm after the immobilization of Ru, which is ascribed to a metal-ligand charge transfer (MLCT) from Ru to BPy.[20] It was confirmed that $RuCl_2(bpy)(CO)_2$ has the same MLCT band at 410 nm, where $[RuCl_2(CO)_3]_2$ provides no absorption band, which indicates the complexation between BPy units of BPy-PMO and Ru for **1**.

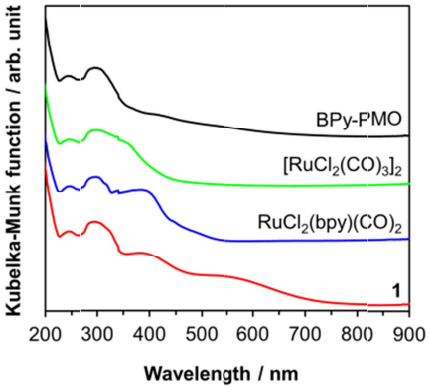


Figure 3. UV-vis DRS spectra for BPy-PMO (black), $[RuCl_2(CO)_3]_2$ (green), $RuCl_2(bpy)(CO)_2$ (blue), and **1** (red)

IR was employed to characterize the carbonyl groups on the same materials as shown in Figure 4. BPy-PMO showed no peaks derived from C–O stretching vibrations. The precursor to **1**, $[RuCl_2(CO)_3]_2$, showed two peaks at 2110 and 2160 cm^{-1}, which are assigned to symmetric and asymmetric C–O stretching vibrations.[21] **1** exhibited two strong peaks at 2075

and 2012 cm^{-1} for CO ligands of the immobilized Ru complex. This red-shift is due to an increase of the back-donation from Ru to CO by reducing the number of CO ligands from three to two (see Scheme 1) and coordination of an electron-donating ligand, BPy.

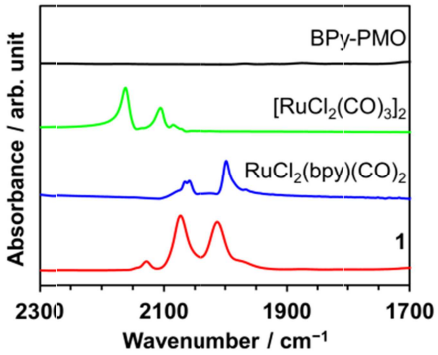


Figure 4. IR spectra of BPy-PMO (black), $[RuCl_2(CO)_3]_2$ (green), $RuCl_2(bpy)(CO)_2$ (blue), and 1 (red).

Ru K-edge XAFS measurements were conducted to reveal the electronic state and structure of the Ru center on **1**. In the X-ray absorption near-edge structure (XANES; Figure 5a), the edge energy of Ru immobilized on BPy-PMO (22119 eV) was in the divalent region and the spectrum was almost identical with that of $RuCl_2(bpy)(CO)_2$. This result indicates that the electronic structures of Ru atoms in **1** and $RuCl_2(bpy)(CO)_2$ are similar. With respect to the extended X-ray absorption fine structure (EXAFS; Figure S5a), EXAFS oscillation (Figure S5b), and its Fourier transforms (Figure 5b), **1** and $RuCl_2(bpy)(CO)_2$ yielded almost the same spectra; therefore, the coordination structure of **1** was analyzed based on the crystallographic data for $RuCl_2(bpy)(CO)_2$.[18] Curve fitting for **1** indicated the presence of Ru–C 1.7±0.3 C atoms at 1.82 Å, Ru–N 1.9±0.4 N atoms at 2.18 Å, and Ru–Cl 1.8±0.2 Cl atoms at 2.42 Å. These results suggest that a similar structure to the corresponding homogeneous complex, $RuCl_2(bpy)(CO)_2$, is successfully formed on the surface of BPy-PMO. It should be noted that no peak corresponding to Ru–Ru was observed around 4 Å in Figure 5b, which means that the Ru centers are isolated on BPy-PMO.

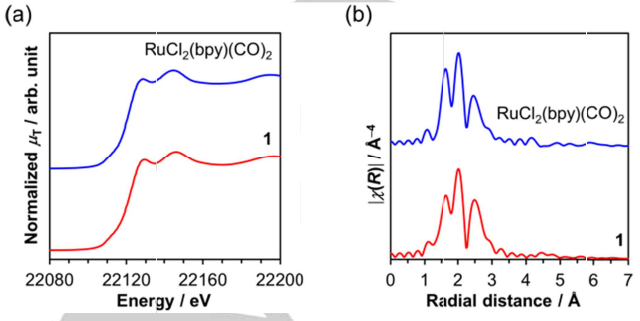


Figure 5. (a) Ru K-edge XANES and (b) Fourier transforms of EXAFS spectra for **1** (red) and $RuCl_2(bpy)(CO)_2$ (blue).

Based on these characterization data, we propose the structure of **1** in Figure 6, in which $RuCl_2(CO)_2$ is immobilized on BPy units of BPy-PMO. The well-defined and isolated Ru species on the pore walls are applicable for selective catalytic reactions.

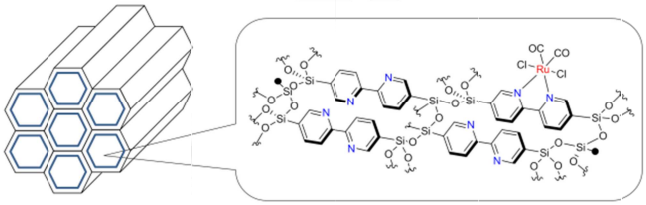
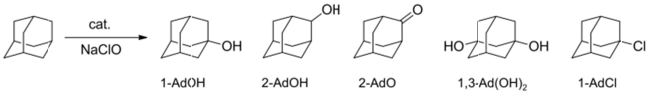


Figure 6. Proposed structure of **1**.

Oxidation of Alkanes over Ru-immobilized BPy-PMO: Selective oxidation of alkanes is an important topic for the efficient utilization of petroleum oil and natural gas.[7-10] Adamantane was used as a model compound to evaluate the catalytic activity and selectivity for this type of oxidation (Scheme 2).[14] This highly symmetric alkane has four equivalent tertiary C–H and twelve equivalent secondary C–H bonds; therefore, the relative selectivity of the active species for tertiary and secondary groups (3°/2°) can be easily determined from Eq. 1. Furthermore, adamantane oxygenates are precursors for the production of photoresists, medicines, and engineering plastics.[14] Some homogeneous catalysts can selectively oxidize the tertiary or secondary C–H bonds of adamantine, such as $RuCl_3$ which has been commercially used for the synthesis of tertiary alcohols;[14 22-27] however, these homogeneous catalysts have drawbacks such as complicated separation and decomposition of the catalysts. In addition, no solid catalyst has achieved good selectivity because of the presence of various catalytic active sites.[28-32] Therefore, the oxidation of adamantane was selected to evaluate the activity, selectivity, and reusability of the PMO-based catalysts.



Scheme 2. Oxidation of adamantane with NaClO.

$$3^{\circ}/2^{\circ} = \frac{(\text{yield of 1-adamantanol})}{(\text{total yield of 2-adamantanol and 2-adamantanone})} \times \frac{12}{4} \quad (1)$$

Ru-immobilized BPy-PMO catalysts were tested for the oxidation of adamantane (substrate/catalyst molar ratio S/C = 50) at 323 K with NaClO as a practical oxidant (Table 1). A control experiment in the absence of a catalyst gave negligible amounts of oxygenated products (entry 1). Ru-immobilized BPy-PMO **3** showed a very low adamantane conversion of 8.1%, as well as a

Table 1. Oxidation of adamantane by Ru catalysts with NaClO.[a]

Entry	Catalyst	Conversion (%)	Yield (%)					3°/2°[b]
			1-AdOH[c]	2-AdOH[c]	2-AdO[c]	1,3-Ad(OH)$_2$[c]	1-AdCl[c]	
1	none	0.3	0.0	0.0	0.0	0.0	0.0	-
2	1	67	44	0.0	2.3	12	0.2	57
3	1-reuse	68	44	0.0	2.5	11	0.2	53
4	2	43	31	0.0	1.7	5.9	0.1	55
5	3	8.1	4.3	0.4	1.0	0.0	1.9	9
6	$RuCl_2(bpy)(CO)_2$	77	45	0.8	2.4	12	1.2	45
7	4	41	25	0.0	1.4	4.4	1.4	54
8	4-reuse	6.1	1.9	1.2	0.1	0.0	0.0	5

[a] Reaction conditions: catalyst (10 mg), adamantane (0.23 mmol), ethylacetate (2.4 mL), and acetate buffer (0.39 mL, pH 4.4, 2 M), reaction temperature (323 K), time of aqueous solution of NaClO (19 mM) supplied at a rate of 27 μL h^{-1} (12 h). [b] 3°/2° = (yield of 1-adamantanol)/(yield of 2-adamantanol and 2-adamantanone)× 3 (see Eq. 1). [c] 1-AdOH (1-adamantanol), 2-AdOH (2-adamantanol), 2-AdO (2-adamantanone), 1,3-Ad(OH)$_2$ (1,3-adamantanediol), 1-AdCl (1-chloroadamantane).

1-adamantanol yield of 4.3% (entry 5). **3** also afforded a significant amount of 1-chloroadamantane (1.9% yield), a typical byproduct in oxidation with NaClO. The new catalyst **1** provided a 67% conversion of adamantane, and the major products were 1-adamantanol (44% yield), 1,3-adamantandiol (12 %; produced by successive oxidation of 1-adamantanol), and 2-adamantanone (2.3%) (entry 2). 2-Adamantanol was produced in less than 0.1% yield due to rapid consecutive oxidation to 2-adamantanone. It is notable that the amount of 1-chloroadamantane was as low as 0.2%. Ru-BPy-PMO catalyst **2**, grafting a commercial catalyst $RuCl_3$, gave a lower adamantane conversion of 43% with a 1-adamantanol yield of 31% (entry 4).[26] We propose that the Ru center in catalyst **1** easily forms coordination bonds with reactant molecules by releasing CO ligands, which results in high catalytic performance for the adamantine oxidation. After the reaction, the Ru centers in **1** are stabilized by the coordination of acetate in solution, and repeatedly available as active sites. In contrast, because of strong coordination of ligands with Ru center in the case of catalyst **2** and **3**, these catalysts show less activity for the reaction than catalyst **1**. Thus, we focused on the catalysis of **1**. For the reaction of **1** in entry 2, a turnover number of Ru for oxygenation was calculated to be 35, which indicates that **1** acts as a catalyst for the oxidation of adamantane. The 3°/2° ratio is 57, so that a tertiary C–H bond was oxidized 57 times faster than a secondary C–H bond. A time-course experiment showed that the 3°/2° ratio remained almost constant (Figure S6). This is the highest regioselectivity ever reported for a heterogeneous catalyst (2–20).[28-32] The result indicates that no radical chain reactions (3°/2° < 15)[33] occur and active electrophilic oxygen species are selectively formed on Ru sites.[8] Moreover, **1** maintained the catalytic activity and selectivity in a reuse experiment; the catalyst produced 1-adamantanol in 44% yield with a 3°/2° ratio of 53 (entry 3). We have verified that the amount of Ru loading was maintained after the oxidation reaction EDX measurements. $RuCl_2(bpy)(CO)_2$ was tested as a homogeneous model of **1**, which afforded 1-adamantanol (45% yield), 1,3-adamantandiol (12%), 2-adamantanol (0.8%), and 2-adamantanone (2.4%) (entry 6). Thus, **1** was as active as $RuCl_2(bpy)(CO)_2$, which suggests there is no diffusion limitation for **1** due to the large pores that allow quick diffusion of the bulk substrate (adamantane, 0.7 nm diameter). The 3°/2° ratio for $RuCl_2(bpy)(CO)_2$ of 45 was slightly lower than that for **1** (57), and the homogeneous catalyst also produced a larger amount of 1-chloroadamantane (1.2%) than **1** (0.2%). Thus, **1** improved the product selectivity compared with the homogeneous counterpart, presumably due to the site-isolation of Ru species for **1**.

The good durability of **1** could be ascribed to the rigid fixation of the Ru species on the pore wall. To provide evidence for this hypothesis, an analog of **1** was examined using MCM-41 bearing BPy groups via butyl group linkers (denoted **4**; Figure S7). MCM-41 is also an ordered mesoporous material with a similar pore diameter (3.4 nm) but consists of pure silica with an amorphous wall structure. Therefore, a linker is necessary to immobilize Ru and it provides mobile Ru sites.

Catalyst **4** showed a similar 3°/2° ratio (54, entry 7) to that for **1**. However, **4** had lower catalytic activity due to quick deactivation, which was clearly observed in the catalyst reuse experiment (almost no activity, entry 8). The catalyst was decomposed by its own active oxygen species and significant leaching of Ru was observed (82%). Thus, we propose that the direct immobilization of Ru complexes on BPy groups within the

framework of BPy-PMO gives a rigid structure, thereby achieving better durability of the catalyst.

Catalyst **1** was then applied for the oxidation of *cis*-decalin to evaluate the stereospecificity of the catalytic system (Scheme 3), because stereospecific oxidation is important for the synthesis of fine chemicals and medicines such as steroids and terpenes.[10,17] The reaction was performed under the same conditions as that for the oxidation of adamantane. **1** gave a 70% conversion of *cis*-decalin and a 63% yield of *cis*-9-decalol with complete retention of the substrate configuration. Thus, no *trans*-9-decalol was detected (<0.1%) and the only byproducts were secondary oxygenates such as *cis*-1-decalone. This result indicates that Ru catalyst **1** directly inserts an oxygen atom into a C–H bond with no free radical reaction, which gives a mixture of *cis*-9-decalol and *trans*-9-decalol via sp^2 carbon radical intermediates.[15,34] Moreover, the activity of the reuse catalyst was compared with that of the fresh catalyst at 50% conversion of *cis*-decaline (Figure 7). Catalyst **1** was reusable and maintained the activity and selectivity for the stereospecific oxidation of tertiary C–H bonds. The direct insertion of oxygen is also important for good durability, because free radicals would randomly attack the catalyst in addition to the substrate.

Scheme 3. Oxidation of *cis*-decalin by **1** with NaClO.

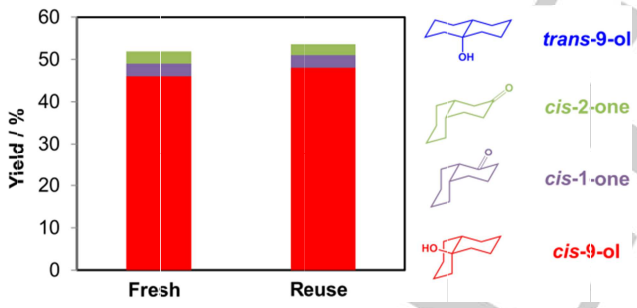


Figure 7. Reuse tests with catalyst **1** for the oxidation reaction of *cis*-decalin. Reaction conditions: catalyst (10 mg), adamantane (0.23 mmol), ethylacetate (2.4 mL), and acetate buffer (0.39 mL, pH 4.4, 2), reaction temperature (323 K), time of aqueous solution of NaClO (19 mM) supplied at a rate of 27 µL h^{-1} (12 h). Denotation: *cis*-9-ol (*cis*-9-decalol), *cis*-1-one (*cis*-1-decalone), *cis*-2-one (*cis*-2-decalone), *trans*-9-ol (*trans*-9-decalol).

Conclusions

Ru species were immobilized in an isolated form directly on 2,2'-bypyridine groups in the BPy-PMO framework. The coordination structure of the immobilized Ru species was similar to that of the corresponding Ru complex, $RuCl_2(bpy)(CO)_2$. The Ru-immobilized PMO was applied for the catalytic oxidation of adamantane using NaClO as an oxidant and high selectivity toward the oxidation of tertiary C–H bonds was observed in addition to catalyst recyclability. Ru-immobilized PMO also selectively oxidized tertiary C–H bonds of *cis*-decalin with perfect retention of its configuration. From these results, we propose that the rigid structure of Ru sites is essentially beneficial to achieve good durability. Furthermore, catalytically controlled oxidation, due to the well-designed isolated metallic sites, emphasizes the potential of the structural advantage.

Experimental Section

Reagents: $[RuCl_2(CO)_3]_2$ was purchased from Sigma-Aldrich, and dehydrated tetrahydrofuran (THF) was obtained from Kanto Chemical Co. Other reagents were of the highest grade and were used without purification.

Synthesis of Ru-immobilized BPy-PMO: BPy-PMO was synthesized according to the literature method, using 5,5'-bis(triisopropoxysilyl)-2,2'-bipyridine as a monomer and octadecyltrimethylammonium chloride as a surfactant.[6] A Ru-immobilized BPy-PMO, denoted **1**, was prepared from BPy-PMO and $[RuCl_2(CO)_3]_2$ as follows. BPy-PMO (100 mg) was added to a THF solution (30 mL) of $[RuCl_2(CO)_3]_2$ (100 mg, 0.50 mmol) under Ar, and the mixture was magnetically stirred under reflux conditions for 3 h. The resulting solid was filtered, washed with THF, and dried at 298 K *in vacuo*, to afford **1** (110 mg) as a brownish powder. A model complex for **1**, $RuCl_2(bpy)(CO)_2$, was synthesized according to a procedure in the literature,[18] and purified by recrystallization. Immobilization of Ru complexes on BPy-PMO was also conducted using other Ru precursors, $RuCl_3{\cdot}xH_2O$ and $RuCl_2(bpy)_2{\cdot}2H_2O$, to obtain the Ru-immobilized BPy-PMOs, denoted as **2** and **3**, respectively (Figure 1). Ru-immobilized BPy-PMO **3** was reported previously.[6] The synthesized materials were analyzed and characterized using ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS; Jasco, V-650), Fourier transform infrared spectroscopy (FT-IR; Perkin-Elmer, Spectrum 100, transmission mode, triglycine sulfate (TGS) detector with a 1 cm^{-1} resolution, 16 times integration), X-ray absorption fine structure (XAFS; at the BL14B2 of SPring-8), energy dispersive X-ray spectroscopy (EDX; Shimadzu EDX-720), nitrogen adsorption (BEL, Belsorp-mini II), and X-ray diffraction (XRD; Rigaku, Ultima IV, Cu Kα).

Oxidation Reactions: The substrate (230 µmol), catalyst (10 mg), ethylacetate (2.4 mL), acetate buffer (0.39 mL, pH 4.4, 2.0 M), and a magnetic stirrer were placed into a Pyrex vial (10 mL) equipped with a screw cap. The reaction was performed at 323 K for a designated time with an aqueous solution of NaClO (19 mM) supplied at a rate of 27 µL h^{-1} using a microfeeder (YMC, YSP-201) through a stainless steel needle (0.15 mm diameter) that penetrated the cap. Evolved gas was removed through another needle (0.1 mm diameter). After the addition of NaClO, the mixture was further stirred for 3 h to completely consume the oxidant. Unreacted substrate and products were extracted five times with ethylacetate and hexane and undecane was added into the extract as an external standard. The solution was analyzed using gas chromatography (GC; Shimadzu GC-14B, flame ionization detector) with an HR-1 (0.25 mm diameter, 25 m long) column and an HR-20M (0.25 mm diameter, 30 m long) column. Products were identified by gas chromatography-mass spectrometry (GC-MS; Shimadzu GC2010/PARVUM2, electron ionization) and nuclear magnetic resonance (NMR; Jeol, ECP-400, ^1H 400 MHz) spectroscopy.

Acknowledgements

This study was supported by the Japan Science and Technology Agency (JST) ACT-C. XAFS measurements were conducted at the BL14B2 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2013B1833, 2014B1643, and 2014A1584).

Keywords: adamantane • alkane • oxidation • periodic mesoporous organosilica • ruthenium

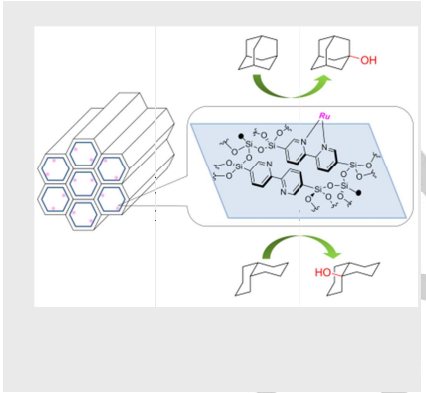
[1] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304-307.
[2] N. Mizoshita, T. Tani, S. Inagaki, *Chem. Soc. Rev.* **2011**, *40*, 789-800.
[3] X. Wang, D. Lu, R. Austin, A. Agarwal, L. J. Mueller, Z. Liu, J. Wu, P. Feng, *Langmuir* **2007**, *23*, 5735-5739.
[4] S. Inagaki, O. Ohtani, Y. Goto, K. Okamoto, M. Ikai, K. Yamanaka, T. Tani, T. Okada, *Angew. Chem.* **2009**, *121*, 4102-4106; *Angew. Chem. Int. Ed.* **2009**, *48*, 4042-4046.
[5] H. Takeda, M. Ohashi, T. Tani, O. Ishitani, S. Inagaki, *Inorg. Chem.* **2010**, *49*, 4554-4559.
[6] M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W. J. Chun, S. Muratsugu, M. Tada, A. Fukuoka, S. Inagaki, *J. Am. Chem. Soc.* **2014**, *136*, 4003-4011.
[7] R. Schlögl, In *Modern Heterogeneous Oxidation Catalysis: Design, Reactions and Characterization* (Ed.: N. Mizuno), Wiley-VCH: Weinheim, **2009**, pp. 1-42.
[8] A. Gunay, K. H. Theopold, *Chem. Rev.* **2010**, *110*, 1060-1081.
[9] J. Yamaguchi, K. Itami, A. D. Yamaguchi, *Angew. Chem.* **2012**, *124*, 9092-9142; *Angew. Chem. Int. Ed.* **2012**, *51*, 8960-9009.
[10] M. C. White, *Science* **2012**, *335*, 807-809.
[11] M. Costas, *Coord. Chem. Rev.* **2011**, *255*, 2912-2932.
[12] B. Meunier, S. P. de Visser, S. Shaik, *Chem. Rev.* **2004**, *104*, 3947-3980.
[13] A. Taguchi, F. Schüth, *Micropor. Macropor. Mater.* **2005**, *77*, 1-45.
[14] K. Chen, L. Jr. Que, *J. Am. Chem. Soc.* **2001**, *123*, 6327-6337.
[15] B. Mortini, *C. R. Phys.* **2006**, *7*, 924-930.
[16] A. A. Spasov, T. V. Khamidova, L. I. Bugaeva, I. S. Morozov, *Pharm. Chem. J.* **2000**, *34*, 1-7.
[17] K. Chen, P. S. Baran, *Nature* **2009**, *459*, 824-828.
[18] M. Haukka, J. Kiviaho, M. Ahlgrén, T. A. Pakkanen, *Organometallics* **1995**, *14*, 825-833.
[19] S. J. Carrington, I. Chakraborty, J.R. Alvarado, P. K. Mascharak, *Inorg. Chim. Acta* **2013**, *407*, 121-125.
[20] A. Gabrielsson, S. Zalis, P. Matousek, M. Towrie, A. Vlcek Jr, *Inorg. Chem.* **2004**, *43*, 7380-7388.
[21] E. Eskelinen, M. Haukka, T. Venalainen, T. A. Pakkanen, M. Wasberg, S. Chardon-Noblat, A. Deronzier, *Organometallics* **2000**, *19*, 163-169.
[22] I. Tabushi, A. Yazaki, *J. Am. Chem. Soc.* **1981**, *103*, 7371-7373.
[23] J. T. Groves, T. E. Nemo, *J. Am. Chem. Soc.* **1983**, *105*, 6243-6248.
[24] I. Yamanaka, T. Gomi, T. Nabeta, K. Otsuka, *Chem. Lett.* **2005**, *34*, 1486-1487.
[25] E. McNeil, J. Du Bois, *J. Am. Chem. Soc.* **2010**, *132*, 10202-10204.
[26] Y. Arai, T. Onozawa, S. Niiyama, K. Yoshida, *JP Pat.* **2008**, 4 171 879.
[27] Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, *J. Org. Chem.* **1996**, *61*, 4520-4526.
[28] I. L. Viana Rosa, C. M. C. P. Manso, O. A. Serra, Y. Iamamoto, *J. Mol. Catal. A: Chem.* **2000**, *160*, 199-208.
[29] C. Nozaki, C. G. Lugmair, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 13194-13203.
[30] A. W. Holland, G. Li, A. M. Shahin, G. J. Long, A. T. Bell, T. D. Tilley, *J. Catal.* **2005**, *235*, 150-163.
[31] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *J. Catal.* **2009**, *267*, 1-4.
[32] S. Ikurumi, S. Okada, K. Nakatsuka, T. Kamegawa, K. Mori, H. Yamashita, *J. Phys. Chem. C* **2014**, *118*, 575-581.
[33] G. Süss-Fink, L. Gonzalez, G. B. Shul'pin, *Appl. Catal. A* **2001**, *217*, 111-117.
[34] H. Kobayashi, I. Yamanaka, *J. Mol. Catal. A: Chem.* **2008**, *294*, 37-42.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Ru species were immobilized in an isolated form directly on 2,2'-bypyridine groups in a PMO framework. The Ru-immobilized PMO oxidizes the tertiary C−H bonds of adamantane with significantly high regioselectivity. Moreover, the catalyst converts *cis*-decalin to *cis*-9-decalol with complete retention of the substrate stereochemistry. The Ru catalyst can be separated by simple filtration and reused without loss of the original activity and selectivity for the oxidation reactions.



*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title