

A Coordinatively Unsaturated Ru Complex Catalyst Supported on SiO₂ Active for Aldehyde Selective Oxidation

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Introduction

Immobilization of metal complexes on support surfaces in a controlled manner is still the state of the art in the assimilative field between homogeneous and heterogeneous catalysis. The potential of immobilized metal-complex catalysts remarkably interplays with the nature of support surface, resulting in significant rate enhancements and novel catalytic performances that homogeneous analogue complexes do not exhibit. We have succeeded in preparing a novel coordinatively unsaturated Ru-diamine complex on a SiO₂ surface, which was characterized by Ru K-edge EXAFS, for selective oxidation of aldehyde using O₂ at room temperature.

Experimental

A SiO₂-supported Ru complex was prepared as illustrated in Scheme 1 [1]. A SiO₂ surface was modified with *p*-styryltrimethoxysilane (A) and its styryl moiety was reacted with Ru-monomer precursor (C) with a styryl group at the surface, forming a supported Ru complex (D) with a saturated Ru center coordinated with a *p*-cymene ligand (Scheme 1). In the presence of O₂ and IBA, the SiO₂-supported Ru complex (D) was transformed into an active unsaturated Ru complex (E) by elimination of the *p*-cymene ligand. The structures of the supported Ru complexes were characterized by Ru K-edge EXAFS at 15 K.

Results and Discussion

Table 1 shows curve-fitting analysis of Ru K-edge EXAFS measured at 15 K for the precursor complex (C), the supported Ru complex (D) and activated Ru complex (E). Similar local coordination was found for (C) and (D), indicating that the supported Ru complex (D) had similar coordination structure to the homogenous precursor (C) as shown in Scheme 1.

The *p*-cymene ligand of (D) was quantitatively eliminated from the Ru site in the presence of IBA and O₂, and an unsaturated Ru complex (E) was produced on the surface. Significant structural changes were observed by UV/VIS and ¹³C solid-state NMR. Ru K-edge revealed that an unsaturated Ru-monomer complex was produced with two coordination bonds of Ru-Cl at 0.234 nm (coordination number = 1.2) and Ru-N at 0.208 nm (CN = 1.6) as shown in Table 1. The formed unsaturated Ru complex was highly active for selective oxidation of aldehyde using O₂ at room temperature and Ru K-edge also demonstrated that the unsaturated Ru complex stable and durable under the catalytic reaction.

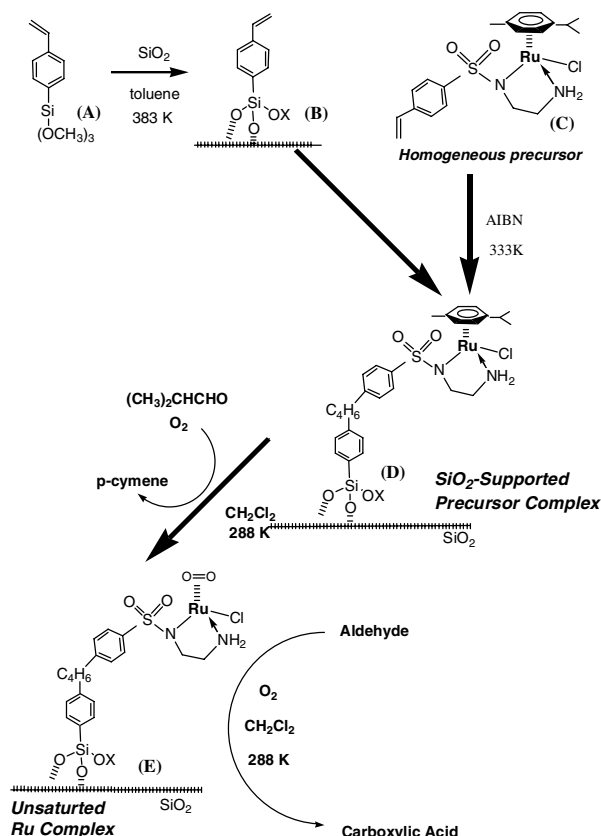
Table 1 Curve fitting results of Ru K-edge EXAFS measured at 15 K

Catalyst	Shell	CN	Distance /nm	σ^2 /nm ²
(C) ^a	Ru-Cl	1.0	0.236	(2±3)x10 ⁻⁵
	Ru-N	2.0	0.213	(-1±2) x10 ⁻⁵
	Ru-C	6.0	0.227	(2±24)x10 ⁻⁵
(D) ^b	Ru-Cl	1.0	0.238	(2±2)x10 ⁻⁵
	Ru-N	2.0	0.215	(0±1) x10 ⁻⁵
	Ru-C	6.0	0.230	(18±39)x10 ⁻⁵
(E) ^c	Ru-Cl	1.2±1.0	0.234	(1±5)x10 ⁻⁵
	Ru-N	1.6±1.2	0.208	(-1±3)x10 ⁻⁵

^a $k=3-14$, $R=1.0-2.2$, $\Delta E_0=9.5$, $R_f=1.74\%$.

^b $k=3-15$, $R=1.3-2.2$, $\Delta E_0=7.8$, $R_f=2.15\%$.

^c $k=3-14$, $R=1.3-2.2$, $\Delta E_0=8.6$, $R_f=1.73\%$.



Scheme 1 Preparation of the unsaturated Ru complex on SiO₂ for aldehyde oxidation.

Reference

[1] M. Tada et al., *Angew. Chem. Int. Ed.* **2007**, 46, 7220

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