

# A Coordinatively Unsaturated Ru Complex Supported on SiO<sub>2</sub> Active for Alkene Epoxidation

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## Introduction

Immobilization of metal complexes onto solid surfaces 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 surfaces, resulting in significant rate enhancements and novel catalytic performances that homogeneous analogue complexes do not exhibit. We have succeeded in the preparation of a Ru complex with *p*-cymene ligand on a SiO<sub>2</sub> surface and found that isobutyraldehyde (IBA) and O<sub>2</sub> induced the selective elimination of the *p*-cymene ligand from the Ru site. The structures of the SiO<sub>2</sub>-supported Ru complexes were characterized by Ru K-edge EXAFS, which revealed that the formation of a coordinatively unsaturated Ru site active for alkene epoxidation<sup>[1]</sup>.

## Experimental

A SiO<sub>2</sub>-supported Ru-diamine complex (A) (Scheme 1) was prepared by grafting a styryl moiety of a corresponding Ru-complex precursor to SiO<sub>2</sub>-supported *p*-styryl-trimethoxysilane<sup>[1]</sup>. The stoichiometric removal of a *p*-cymene ligand of the supported Ru complex (A) was carried out in CH<sub>2</sub>Cl<sub>2</sub> with an equivalent amount of IBA to Ru under the atmospheric pressure of O<sub>2</sub>.

The local coordination of supported Ru complexes before (A) and after (C) the removal of *p*-cymene was characterized by Ru K-edge EXAFS measured at 15 K and coordination numbers and bond distances were estimated by curve-fitting analysis of EXAFS Fourier transforms using UWXAFS and FEFFIT programs.

## Results and Discussion

Table 1 shows the coordination numbers and bond distances for the supported Ru complex with *p*-cymene ligand (A) and the Ru complex after the elimination of the *p*-cymene ligand (C) in Scheme 1. FT-IR, UV/VIS, and Ru K-edge EXAFS showed that the structure of the supported Ru complex (A) was similar to that of the precursor complex before the immobilization onto SiO<sub>2</sub>. The local coordination of (A) was a saturated structure coordinating a *p*-cymene ligand as shown in Table 1.

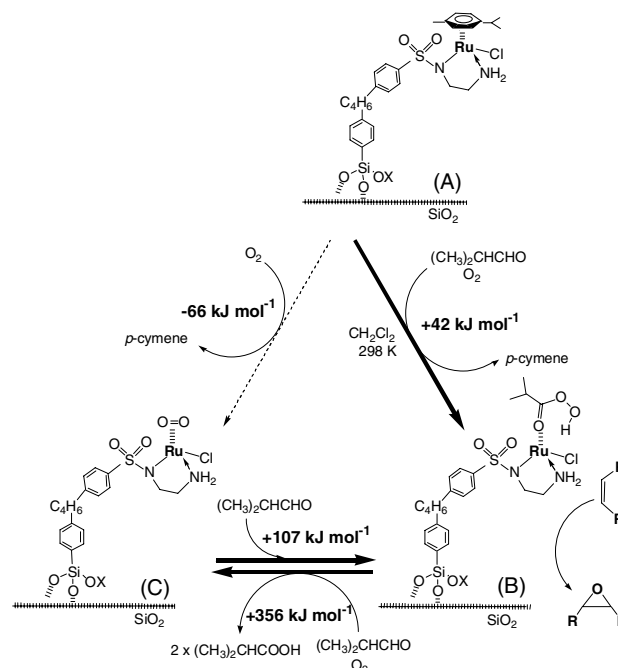
After the reaction with IBA and O<sub>2</sub>, significant structural changes were observed by UV/VIS and the stoichiometric amount of *p*-cymene was detected in a solution phase, indicating that the selective elimination of the *p*-cymene ligand. Two bonds of Ru-Cl at 0.234 nm and Ru-N at 0.207 nm were observed, whose coordination numbers were 1.3 and 2.2, respectively. There was no

metal-metal bond on the supported Ru complexes. The coordination numbers indicated that the formation of the coordinatively unsaturated Ru complex on SiO<sub>2</sub>, which was active species for selective alkene epoxidation. The detail structures of the unsaturated Ru complexes were modeled by DFT calculations based on the structural parameters of Ru K-edge EXAFS as shown in Scheme 1.

Table 1: Curve-fitting analysis of Ru K-edge EXAFS measured at 15 K for the SiO<sub>2</sub>-supported Ru catalyst before and after the activation with IBA and O<sub>2</sub>.

Catalyst activation	Shell	CN	Distance/nm	$\sigma^2$ /nm <sup>2</sup>
(A) <sup>a</sup>	Ru-Cl	1.0	0.236	3
	Ru-N	2.0	0.214	0
	Ru-C	6.0	0.226	13
(C) <sup>b</sup>	Ru-Cl	1.3	0.234	5
	Ru-N	2.2	0.207	1

<sup>a</sup>  $k=30-140$  nm<sup>-1</sup>,  $R=0.10-0.22$  nm. <sup>b</sup>  $k=30-140$  nm<sup>-1</sup>,  $R=0.13-0.24$  nm.



Scheme 1 The structures of SiO<sub>2</sub>-supported Ru-complex catalysts for selective alkene epoxidation.

## Reference

[1] M. Tada et al., *Angew. Chem. Int. Ed.* in press.

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