

## XAFS Characterization of Oxide-Surface Supported Pd Complexes for Alkene Hydroamination

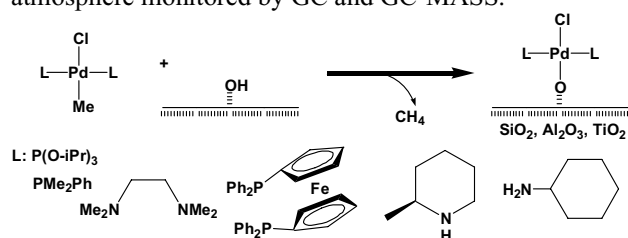
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### Introduction

Amine derivatives, which are valuable and important chemicals, have been produced via several synthetic processes. The direct synthesis of a new C-N bond by the addition of an amine to an unsaturated C-C bond, hydroamination, is of great significance. However, this reaction is generally slightly exothermic and entropically negative, and the hydroamination of alkenes is highly difficult compared to that of alkynes because of the lower electron density of C=C bonds than C-C bonds. We have succeeded in the preparation of oxide-surface supported Pd complexes for the catalytic intrahydroamination of 3-amino propanol vinyl ether to produce the corresponding cyclic amine. This is the first heterogeneous catalyst for alkene hydroamination [1].

### Experimental

Some new Pd monomers with Pd-P or Pd-N bonds were supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> as shown in Scheme 1. The structures of the supported Pd complexes were characterized by XRF, XPS, GC, and EXAFS. Pd K-edge EXAFS spectra were measured at BL-10B station in a transmission mode at 15 K. Background subtraction was conducted by the AUTOBK program, and Fourier-transformed spectra ( $k=30-140 \text{ nm}^{-1}$ ,  $R=0.12-0.24 \text{ nm}$ ) were fitted in R space by FEFFIT program. The catalytic hydroamination of 3-amino propanol vinyl ether was carried out in toluene at 343 K under a nitrogen atmosphere monitored by GC and GC-MASS.



Scheme 1 Preparation of the oxide-supported Pd complexes for alkene hydroamination.

### Results and Discussion

The CH<sub>3</sub> groups selectively reacted with surface OH groups to evolve CH<sub>4</sub>. The N and P ligands of the precursors did not dissociate into the solution during the attaching reaction. The chlorine ligands remained on Pd as estimated by the intensity ratios of XPS Cl2p and Pd3d peaks for both Pd-P and Pd-N complexes.

The curve-fitting analysis for the Pd K-edge EXAFS Fourier-transformed spectra of the Pd-P complexes

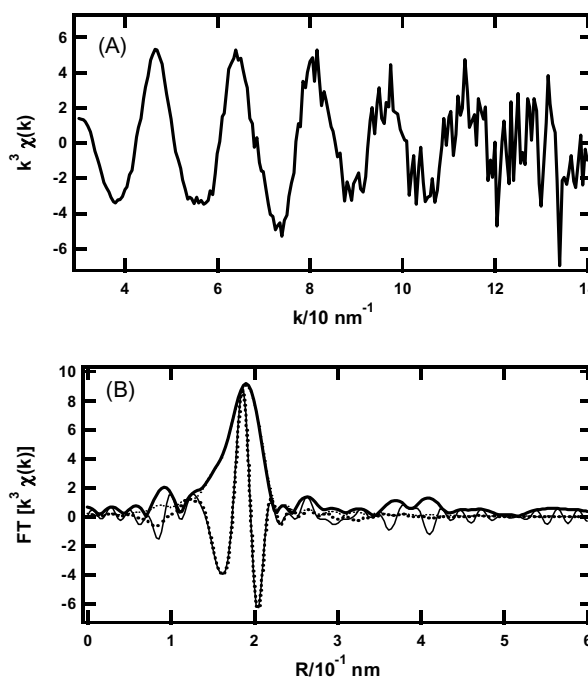


Figure 1 A Pd K-edge EXAFS oscillation (A) and its Fourier-transformed spectra (B) for the supported Pd-P(O-iPr)<sub>3</sub> complex on a SiO<sub>2</sub> surface.

revealed that the existence of a Pd-O bond at 0.212 nm (CN=0.8) and Pd-P(Cl) bonds at 0.235 nm (CN=3.1) (Fig. 1). The bond distances in the Pd-N complexes supported on SiO<sub>2</sub> (Pd-N(O): 0.213 nm and Pd-Cl: 0.235 nm) were similar to those in the supported Pd-P complexes. The results demonstrate a similar bonding feature in the coordination sphere around Pd in the catalysts derived from both precursors.

The supported Pd catalysts exhibited high catalytic activity for the alkene hydroamination. No changes in the coordination numbers and bond distances around the Pd center after the catalytic reaction was observed by EXAFS curve-fitting, suggesting that the supported Pd complexes are not only active but also durable for the catalytic hydroamination.

### References

- [1] M. Tada, M. Shimamoto, T. Sasaki, and Y. Iwasawa, *Chem. Commun.*, 2562 (2004).

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