# Structure of new rhodium catalysts prepared by surface molecular imprinting method

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### Introduction

Surface molecular imprinting is a promising method to prepare molecular recognizing catalysts. Using this method, we have prepared a rhodium catalyst, which is active for olefin hydrogenation. The catalyst recognizes the fine difference of reactants and the activity is enhanced by forming silica over layers [1]. In this study, we have measured EXAFS to elucidate the reason for the ability of molecular recognition and the activity enhancement.

### Experimental

Sample preparation: $SiO_2$ (Ox50, Degussa, preevacuated at 673 K, 1 h) was impregnated with a hexane solution of $Rh_2Cl_2(CO)_4$. Then excess $P(OCH_3)_3$ was added to the supported rhodium compound in diethyl ether followed by evacuation at 363 K for 3 h ($Rh_{sup}$). After that, $Si(OCH_3)_4$ and water vapors were condensed on the $Rh_{sup}$ catalyst surface at room temperature followed by hydrolysis at 348 K for 7 h and evacuated at 363 K for 12 h to form $SiO_2$-matrix overlayers ($Rh_{imp}$).

EXAFS measurement and analysis: Rh K edge EXAFS for the Rh catalysts were recorded at BL-10B at 10-15 K with a transmission mode. After background subtraction, $k^3$ weighted EXAFS functions were Fourier transformed into a R-space and a curve fitting analysis was carried out in the R-space using the FEFFIT program [2]. The k and R ranges for the Fourier transformation and curve fitting were 30—140 nm$^{-1}$ and 0.12—0.29 nm, respectively. Backscattering amplitudes and phase shifts were calculated by the FEFF8 code [3].

### Result and discussions

Figure 1 (a) and (b) show FT of $k^3$ weighted EXAFS functions of $Rh_{sup}$ and $Rh_{imp}$.. Table 1 shows the result of curve fitting analysis for $Rh_{sup}$ and $Rh_{imp}$. After dosing $P(OCH_3)_3$, Rh—O and Rh—P bondings were observed at 0.203 and 0.224 nm with coordination numbers of 1.6 and 2.3. The result suggests that the Rh species after dosing of $P(OCH_3)_3$ were coordinated by two surface oxygen atoms and two $P(OCH_3)_3$ ligands. When the silica overlayer was deposited on the surface by a hydrolysis reaction of Si(OMet)$_4$, Rh—Rh bondings were formed and half of $P(OCH_3)_3$ was removed. The result suggests that the pore in which the Rh species exist shrank by the hydrolysis reaction and that the attached $(Rh(P(OCH_3)_3)_2O(s)_2)_2$ was pressed by the silica wall, which results in the formation

of a Rh—Rh bonding and elimination of two $P(OCH_3)_3$ ligands. Thus, $Rh_{imp}$ catalyst is Rh dimer species coordinated by two surface oxygen atoms and a $P(OCH_3)_3$ ligand each. By exposing $Rh_{imp}$ catalyst to hydrogen, Rh—Rh distance decreased to be 0.265 nm and when the catalyst after exposed to $H_2$ react with 3-methyl-2-pentene, the Rh—Rh distance increased reversibly to 0.270 nm. The result suggests that the hydrogenation reaction is associated by the cycle of shrinking and expansion of the Rh—Rh bond.
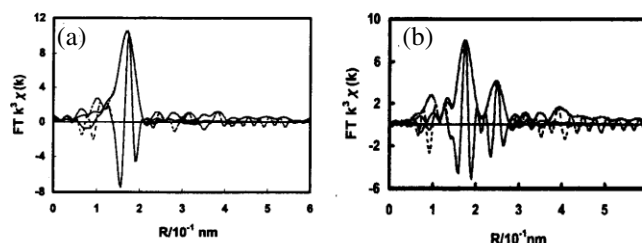


Figure 1. Fourier transformed EXAFS functions ($k^3\chi(k)$) for (a) $Rh_{sup}$ and (b) $Rh_{imp}$.

Table 1. Structural parameters delivered by curve fitting analysis.

| Sample/Shell | CN | R/nm | $\sigma^2$/10$^{-5}$ nm$^2$ | $\Delta E_0$/eV, Rf(%) |
|---|---|---|---|---|
| $Rh_{sup}$ | | | | |
| Rh-O | 2(1) | 0.203(3) | 6(3) | 6(4) |
| Rh-P | 2(1) | 0.224(5) | 2(2) | 0.2 |
| $Rh_{imp}$ (fresh) | | | | |
| Rh-O | 2.0(5) | 0.211(2) | 4(3) | 11(2) |
| Rh-P | 1.1(2) | 0.221(1) | 1(2) | 1.4 |
| Rh-Rh | 1.3(3) | 0.268(1) | 7(1) | |

### References
[1] M. Tada, T. Sasaki, T. Shido, and Y. Iwasawa, *J. Phys. Chem.* submitted.
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[3] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, *Phys. Rev. B* **58**, 7565 (1998).