

XAFS study on phenoxyethoxymethyl-polystyrene (PEM)-based novel microencapsulated osmium oxide catalyst

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Introduction

Osmium-catalyzed dihydroxylation of olefins is one of the most efficient methods for the preparation of vicinal diols. Recently, a new catalyst, phenoxyethoxymethyl-polystyrene (PEM)-based polymer-supported osmium oxide catalyst (PEM-MC Os catalyst) [1], was developed based on a microencapsulation (MC) technique. The catalyst successfully proceeds asymmetric dihydroxylation of olefins using bisinchona alkaloids as a chiral legand and $K_3Fe(CN)_6$ as a cooxidant in H_2O /acetone, and easily recovered by filtration and reused without loss of activity several times. In order to elucidate the active site structure of the catalyst, in the present study, we applied X-ray absorption technique to investigate the electronic state and local structure of Os species in the catalyst.

Experimental

The Os L_{III} -edge XAFS measurement was performed at room temperature in transmission mode at the BL-10B station [2] of KEK-PF, Tsukuba, Japan, with a Si(311) channel-cut monochromator. The sample was sealed with a polyethylene film in a dry atmosphere. Normalization of XANES and data reduction on EXAFS were carried out as described elsewhere [3].

Results and discussion

For the Os L_{III} -edge XANES of PEM-MC Os catalyst, the position of white line was close to that for OsO_2 and K_2OsO_4 (Fig. 1), indicating that the starting material, OsO_4 , was reduced to Os^{6+} or Os^{4+} ions during the preparation procedure. The figure of the XANES for the catalyst was similar to that for OsO_2 except for the intense white line.

To clarify the local structure around the Os atoms in the catalyst, we performed nonlinear curve-fitting analyses of the Fourier-filtered EXAFS of the first and the second shells around Os atoms by a least-squares method. The Os-O (or Os-C) shell was empirically extracted from the EXAFS of OsO_4 . The results are listed in Table 1. The coordination numbers (CN) and interatomic distances (R) for short and long Os-O bonds in the catalyst were estimated as ca. 2 and 1.85 Å, and ca. 4 and 2.01 Å, respectively, similar to those in the OsO_2 reference sample. This suggests that Os ions in the catalyst have similar local structure to that in OsO_2 . The higher white line intensity mentioned above suggest that the OsO_2 species in polymer are more cationic or more

symmetric than that in the bulk OsO_2 as they are highly dispersed in polymer.

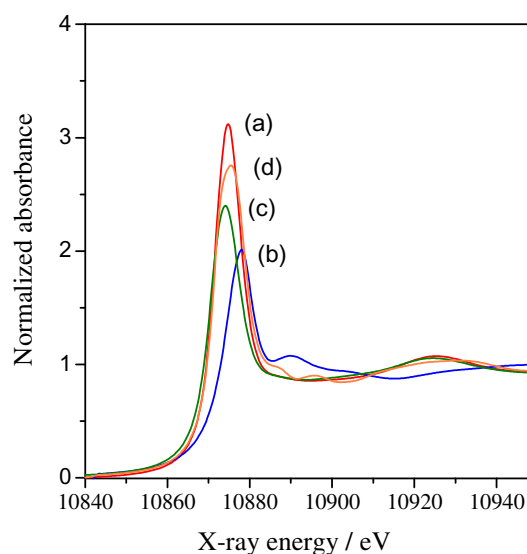


Fig. 1: Os L_{III} -edge XANES of (a) PEM-MC Os catalyst, (b) OsO_4 , (c) OsO_2 and (d) $K_2OsO_4 \cdot 2H_2O$.

Table 1: Results of curve-fitting analyses

sample	shell	CN	R / nm	$\Delta\sigma^2$
PEM-MC Os catalyst	Os-O(C)	2.5	0.185	-0.00460
	Os-O(C)	4.2	0.201	-0.00244
OsO_2	Os-O(C)	2.0	0.349	-0.00098
	Os-O(C)	2.1	0.186	-0.00292
	Os-O(C)	4.1	0.200	-0.00070
OsO_4	Os-O(C)	2.0	0.344	-0.00007
	Os-O(C)	4	0.170	0

$\Delta\sigma^2$: difference of Debye-Waller factor from that for OsO_4 .

References

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