

Local Structure of Br in Brominated Mesoporous Ethylenesilica

Tomohisa MIYAJIMA¹, Koujiro NAKAI¹, Hideaki YOSHITAKE*¹
¹Yokohama National University, Yokohama 240-8501, Japan

Introduction

Recently-developed periodic mesoporous organosilica (PMO) has been considered as a soft material in a new category. In fact, PMO is signalized by its intermediate properties between an organic polymer and amorphous silica. In the bromination of C=C double bonds in mesoporous ethylenesilica at room temperature, considerable number of double bonds in the bulk are reacted, suggesting bromine diffuses into the bulk where nitrogen cannot penetrate at 77 K. Since the product can be further converted by another organic reaction, the local structure of Br is significantly important. For this reason, we investigated Br K-edge EXAFS in this product.

Experiment

XAFS spectra were measured using Beamline 9A. The spectra were acquired three times at 293 K, and the average $\chi(k)$ was calculated from the extracted spectra. A standard automated data reduction procedure was used to extract the experimental EXAFS spectra using a REX 2000 (Rigaku Co.) program assembly. The amplitudes and phase-shift functions were calculated using the FEFF code.

Results and Discussion

The figure shows the $k^3\chi(k)$ EXAFS oscillation, the radial distribution function and the curve-fitting result of brominated ethylenesilica. The first peak around 1.5 Å is clearly assigned to the Br-C bond (fig (b)). However, the second largest peak around 2.8 Å is assigned to a sum of the scattering of the next nearest neighbors of C and Si. The curve-fitting results are summarized in the table. The coordination number for these three atoms is nearly unity, and is consistent with the structure of a brominated C=C double bond where each carbon is bound to a silicon atom.

The appearance of the first shell as a strong peak reveals the uniformity in Br-C bond, suggesting that there is sufficient space around the C=C double bonds for the Br₂ addition reaction without resulting in considerable stereochemical distortion. The lack of a peak from Br-Br bond in the Fourier transform provides an evidence for that the large uptake of bromine in the bromination (< 40%) is not due to molecular Br₂ adsorbed. A tiny peak around 2.1 Å was not able to be fitted with a Br-Br bond.

The Br-C bond length (1.83 Å) is significantly shorter than that in bromoalkanes (ca. 1.9 Å). This length depends on the bond order of the neighboring C-C bond; C-Br bond to an alkynyl carbon is shorter than to an alkenyl carbon, and that to the alkenyl group is shorter than to an alkyl carbon. The Br-C distance found in the table is close to that in bromobenzene (1.8674 Å), suggesting a similar characteristic of Br-C with that to an aryl C.

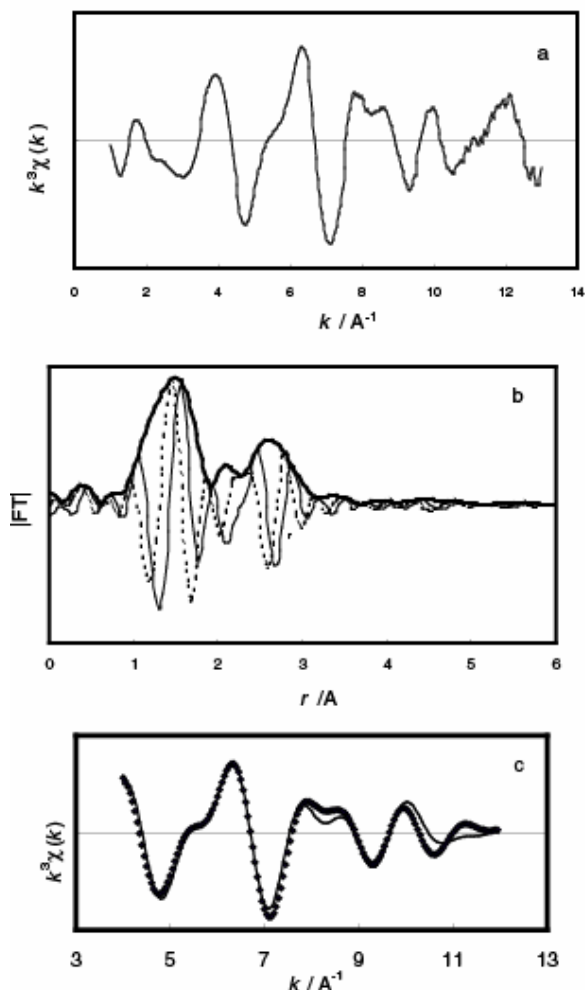


Figure Br EXAFS of brominated ethylenesilica. (a) $k^3\chi(k)$, (b) Fourier transform and (c) curve-fitting of the inversely-Fourier transformed spectrum at $r = 0.9 - 3.2 \text{ Å}$.

Table : Curve-fitting results for the Br K edge EXAFS.

scatterer	$\gamma/\text{Å}$	N	ΔE_0 / eV	$\sigma/\text{Å}$
C	1.829	0.82	15.4	0.109
C	3.077	1.00	5.19	0.089
Si	3.095	0.82	-3.73	0.180

γ : bond distance, N : coordination number, ΔE_0 : shift of the energy threshold, and σ : Debye-Waller factor.

*yos@ynu.ac.jp