

C K-edge XAFS measurements for detection of unsaturated bonds in organically bridged silica materials

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Introduction

Microporous organosilica membranes are attractive because of unique features such as a high surface area, improved hydrothermal stabilities, and applications of them are widely expanding [1]. Most of researches have been focused on bis-(triethoxysilyl)ethane (BTESE) and characteristics of BTESE derived materials. To expand the possibilities of organosilica membranes we have been exploring different precursors to introduce ethylene and acetylene bridges into the organosilica membranes. Though the properties of the synthesized organosilica were characterized by the many analytical methods, there exists no method that provide the evidence of the unsaturated carbon bond. Moreover, the quantification of the amount of the unsaturated bonds is quite difficult. We have utilized C K-edge XAFS spectroscopy for detecting remained unsaturated bonds in PMOs, and the possibilities of quantification will be discussed.

2. Experimental

2.1 Samples

Table 1 shows precursors used for synthesis of organically bridged silica materials. Three types of precursor were utilized including bis-(triethoxysilyl)ethane, bis-(triethoxysilyl)ethylene and bis-(triethoxysilyl)acetylene, and their ethoxysil groups were converted into siloxane or silanor groups via the hydrolysis and polymerization. Ethanol solutions of samples (5 wt %) were prepared for each, and a 30 μ L of the solution was dropped three times onto a Si substrate of approximately 15 mm square under atmospheric condition.

TABLE 1. Samples and their precursors of the organically bridged silica materials investigated.

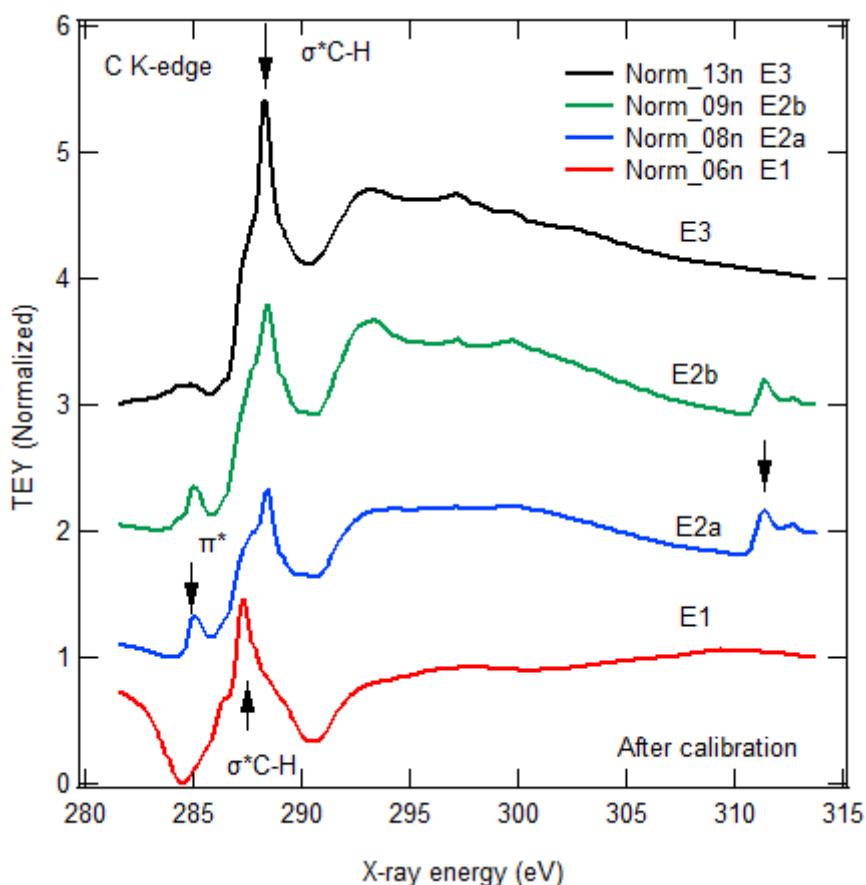
Sample name	Precursor	Approximate mass fraction of carbon
BTES-E1 ethane bridge	$(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$	18.17 %
BTES-E2 ethylene bridge	$(\text{EtO})_3\text{SiCHCHSi}(\text{OEt})_3$	18.45 %
BTES -E3 acetylene bridge	$(\text{EtO})_3\text{SiCCSi}(\text{OEt})_3$	18.74 %

2.2 XAFS measurements

Experiments were carried out on the beamline BL13 [2]. Incident X-rays were monochromatized with a grating monochromator, and the incident X-ray intensity was monitored from a Au coated grid of stainless steel. The beam size at the sample position was approximately 1 mm square, and the glancing angle of 20 deg. was employed for X-ray absorption fine structure (XAFS) measurements. Total electron yield (TEY) from a sample was monitored, and the normalized spectra were utilized for the further analysis. To avoid the inhomogeneity of the sample on the substrate, several positions on the sample were selected for measurements. Incident X-ray energy was calibrated with the main peak obtained with PMMA, and the observed spectra were shifted to 1.44 eV minus to let the peak energy of PMMA be 288.34 eV.

3. Results and discussion

Figure 1 shows C K-edge XAFS spectra of organically bridged silica materials. Obtained main peak with ethane bridged silica material (BTES-E1) showed a main peak around 290.2 eV, and the spectrum was almost identical to that obtained with the blank (Si substrate). On the other hand two spectra of ethylene bridged silica material (BTES-E2) showed the characteristic peak around 285.04 eV. The peak energy was similar to the reported value of 1s to π^* transition (around 285 eV) obtained from the adsorbed ethylene on the Si substrate [3]. Though the similar peak corresponding to 1s to π^* transition was expected with acetylene bridged silica, no clear peak was observed while the broadened peaks remained in the present experiment. It was clear that the direct evidence of the remaining unsaturated carbon bond in the organically bridged silica material could be monitored with the C K-edge XAFS spectroscopy. While the contribution of the surface contamination with the hydrocarbon should be considered for determination of the portion of the unsaturated bond in the sample.



REFERENCES

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