

Coordination of Cu²⁺ to ethylenediamine-functional ligands densely packed in interlayer of polysilsesquioxane

Hideaki YOSHITAKE*, Hitomi NAKAJIMA
Yokohama National University, Yokohama 240-8501, Japan

Introduction

The functionalization have been extensively studied for mesostructured silicas with a large surface area.[1] The density of organic functions is an important parameter for such materials, because they work generally as active sites and, therefore, enormous efforts have been dedicated to increase the density. A stable functionalized silica at the end of this enlargement can be polysilsesquioxane, (R-SiO_{1.5})_n, which contains one organic function par Si atom.[2] The structure of this material is characterized mainly by two-dimensional ultra thin layer of "silica" with highly packed organic functions. Since the spacing between functions is quite small, the local structure of transition metal cation captured by the functional group can be significantly different from those on conventional functionalized silicas. We report here XANES spectra of Cu²⁺ coordinated with en (ethylenediamine) ligand, in (NH₂CH₂CH₂NHCH₂CH₂CH₂SiO_{1.5})_n.

Experiment

The material was hydrothermally synthesized with 3-(2-aminoethyl)aminopropyltriethoxysilane (AeAPTES), hexadecylsuccinic acid (C16SA) anhydride, tetraethyl orthosilicate (TEOS) and 1-hexadecanol (C16OH) with keeping AeAPTES: C16SA= TEOS: C16OH = 1:1. All solids synthesized in AeAPTES/TEOS = ∞ ~ 0.111 provide lamellar patterns in XRD. The adsorption of Cu²⁺ was carried out in aqueous solution of cupric chloride.

The Cu K-edge XANES spectra were measured in a transmission mode.

Results and Discussion

The adsorption capacity of Cu²⁺ is summarized with the results of elemental analysis of the polysilsesquioxane in Table 1. The amount of nitrogen and, consequently, that of en decreases with increasing TEOS in the sol. In contrast, the stoichiometric relation with Cu is suddenly changed AeAPTES: TEOS between 4: 6 and 3:7. N/ Cu is around 0.25 at the high AeAPTES (viz. high en) region, while it increases to 0.43 at the low AeAPTES (viz. low en) region. These ratios imply the coordination number of en to Cu²⁺: Cu(en)₂ and Cu(en) for AeAPTES: TEOS ≥ 4: 6 and ≤ 3.7, respectively. The lattice constant in XRD is changed simultaneously.

The Cu XANES spectra are depicted in Figure 1. The data for S₁₀₋₀ and 5-5 are almost identical, including a weak pre-edge peak around 8979 eV, which is attributed to the 1s-3d transition in a square-planar coordination. Although the pre-edge peak is still weak, the intensities of

the shoulder peaks at 8989 eV and 8996 eV are reduced in S₃₋₇. The latter two bands have been assigned to 1s-4p transition with a shakedown process and unresolved transitions of 1s-5p with a shakedown and of 1s-4p, respectively. The peak at 8999 eV, assigned to a 1s-5p transition, does not change in intensity. Considering that the transition probability is proportional to the density of unoccupied states, the decrease in the intensity of the absorptions at 8989 and 8996 eV without substantial decrease or increase of the 1s-3d band implies a change of ligands with retention of almost square-planar coordination environment.

Table 1: Cu²⁺ absorption in polysilsesquioxane

AeAPTES: TEOS	N mmol g ⁻¹	Cu ²⁺ mmol g ⁻¹	Cu/ N
10: 0 (S ₁₀₋₀)	4.4	1.10	0.25
9: 1 (S ₉₋₁)	4.3	0.994	0.23
8: 2 (S ₈₋₂)	4.2	1.06	0.26
7: 3 (S ₇₋₃)	4.0	1.07	0.26
6: 4 (S ₆₋₄)	3.8	0.917	0.24
5: 5 (S ₅₋₅)	3.0	0.637	0.21
4: 6 (S ₄₋₆)	3.5	0.894	0.26
3: 7 (S ₃₋₇)	2.6	1.13	0.43
2: 8 (S ₂₋₈)	1.6	0.654	0.41
1: 9 (S ₁₋₉)	0.76	0.323	0.43

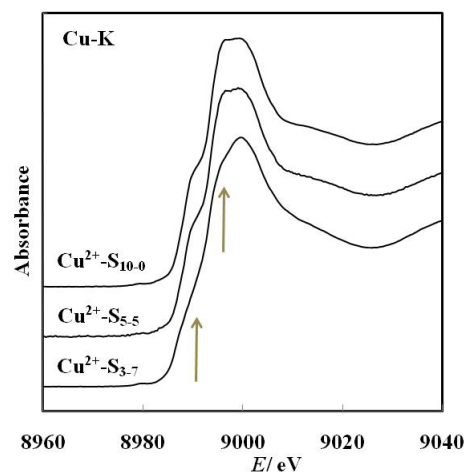


Figure 1 Cu K edge XANES spectra.

References

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* yos@ynu.ac.jp