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Structural Change of Calcium Silicate, a New Type of Desulfurization Material, Studied by Si K Edge XAFS

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Abstract. CaSiO_3 was found to be a material effective for deSO_x in the presence of NO. The material is promising for the solution of environmental problems of exhaust gas from power station. SO_2 was removed as CaSO_4 , involving oxidation of sulfur, accompanied by reduction of NO. After use as a deSO_x reagent, it is confirmed that calcium ions become sulfate form but it has been difficult to examine what form silicon atoms are stabilized as. Q^2 silicon in metasilicate chain may be broken by absorption of SO_x and it is expected that it changes to Q^4 silicon as a silica. However, there has been no direct evidence. In the present work, we recorded Si K edge XAFS of CaSiO_3 before and after use at UVSOR, Okazaki, Japan. The XANES spectra suggested the formation of Q^4 silicon, possibly, forming so-called silica.

1. INTRODUCTION

CaSiO_3 was found to be a material effective for deSO_x in the presence of NO. [1] The material is promising for the solution of environmental problems of exhaust gas from power stations. SO_2 was removed as CaSO_4 , involving oxidation of sulfur, accompanied by reduction of NO. Ideally, the reaction (desulfurization) proceeds like;

After use as a deSO_x reagent, it is confirmed that calcium ions become sulfate form but it has been difficult to examine what form silicon atoms are stabilized as. It is naturally speculated that silicon ions are present as so-called silica as expressed in equation (1). However, all of the calcium ions are not consumed after passing the gas. Calcium silicate is known to have $\text{Ca}_{1-x}\text{H}_x\text{SiO}_3$ form. Therefore, some of calcium ions should be left as a calcium hydrosilicate as shown in equation (2) or (3).

Since the removal amount of NO is always smaller than that of SO_2 , oxidation by gaseous oxygen expressed in equation (2) was suggested. In any case, Si NMR is often used to examine the state of silicon. However, Si NMR study does not give the clear information, i.e., many intermediate resonance lines make it difficult to identify the silicate forms. Either, the X-ray diffraction technique can not be applied to the sample of amorphous.

Calcium silicate involves metasilicate chains $(\text{SiO}_3)_n^{2-}$ which has a SiO_4 unit possessing two terminal oxygens and two bridging oxygens. Calcium ions are located around the chain surrounded by some water molecules. Although some of the calcium ions are removed, protons can be in place of calcium for the compensation of charge balance to maintain metasilicate chain. Therefore, it has been difficult to examine the phase transition from metasilicate to other phase such as orthosilicate found in silica. In the present work, we recorded Si K edge XAFS of CaSiO_3 before and after use as the deSO_x material to investigate the structural change around silicon atoms.

2. EXPERIMENTAL

2.1 Desulfurization

The calcium silicate sample (500 mg) supplied from Wako Pure Chemical Co. was placed in a differential reactor maintained at 403 K. A mixture gas (SO_2 1000 ppm, NO 1000 ppm, O_2 10%, H_2O 10% and He for balance) was passed through the reactor and the composition of outlet gas was analyzed. In the first 80 min, 100 % of SO_2 was removed and the removal rate decreased gradually. The removal rate of NO was always lower than that of SO_2 . At 5 h on stream, 24 % of SO_2 was removed. After 5 h gas passing, total molar amount of removed SO_2 corresponded to 60 % of calcium ions included in the original sample.

2.2 X-Ray absorption

XAFS experiment was carried out at BL-1A at UVSOR (ring energy 750 MeV and stored current 190 -150 mA) at the institute for Molecular Science, Okazaki, Japan, with an InSb(111) double crystal monochromator. The powder sample was mounted on a scratched Cu plate placed under high vacuum ($< 10^{-7}$ Torr). The signal was measured as a photocurrent. The incident photon intensity was measured as photocurrent rising from Au mesh which permits approximately 80% of X-ray transmission.

The XAFS spectra were normalized as described elsewhere [2]. In this procedure, error in the normalized intensity was estimated to be within 6 %. The deconvolution of the XANES spectrum was carried out successfully with a single arctangent for a continuum absorption and Gaussians for resonance absorption. The use of Lorentzians did not give a satisfactory fit.

3. RESULTS AND DISCUSSION

Figure 1 shows the normalized XANES spectra of the sample before and after use for desulfurization accompanied with that of amorphous silica. Each spectrum shows the similar feature and sharp and a prominent peak found at around 11 eV. The peak for CaSiO_3 virgin sample is much broader than that for silica and it gets sharper by passing the gas as shown in Fig. 1 (b). This sharp and intense absorption is possibly due to atomic-like Si 1s to 3p transition. In case of silica, a silicon atom is located at a center of the regular tetrahedron of oxygen atoms. Therefore, Si 3p orbitals should be degenerated resulting in such a sharp absorption. The deconvolution of the spectrum with Gaussians showed that the full width at half maximum (FWHM) was 1.99 eV. On the other hand, for this absorption found in the spectrum of CaSiO_3 virgin sample, FWHM was estimated to be more than 2.8 eV. The use of two Gaussians gave the more satisfactory fit in the deconvolution procedure. Therefore, this suggests that the broadness of the peak is caused by the split of energy level of Si 3p orbitals in CaSiO_3 virgin sample. The silicon atom in metasilicate chain has two kinds of Si-O bonds, resulting in the split of 3p orbitals. This peak is sharpened in the spectrum of CaSiO_3 sample after use. Hence, we can propose that SiO_4 unit got close to a regular tetrahedron by the gas passing or silica partly appeared in the sample.

In any case, 5 h gas passing does not change all calcium ions from silicate to sulfate. Therefore, CaSiO_3 sample after use should be a mixture and must include CaSiO_3 phase. Therefore, we have attempted to subtract the spectrum of CaSiO_3 virgin sample from CaSiO_3 sample after use multiplied by a pertinent weight. Figure 2 shows the difference spectrum with a subtraction weight of 0.5. Evidently, the spectrum is identical with that of silica, suggesting that 50 % of silicon in the sample after use is stabilized as silica. This is well consistent with the value of the percentage of calcium ions which was changed to sulfate. The result indicates that consumption of SO_2 gas by the calcium silicate sample is accompanied by the formation of silica. Although the reaction is enhanced by the presence of water suggesting the presence of the reaction path (2) or (3), we conclude that hydrosilicate form is not stable and the silicate chains changes easily to the 3-dimensional network of silicate to form so-called silica.

Acknowledgments

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References

- [1] Hattori H., Kanuka N., Kanai R., *unpublished result*.
- [2] Tanaka T., Yamashita H., Tsuchitani R., Funabiki T., Yoshida S., *J.Chem. Soc., Faraday Trans. 1* **84** (1988) 2987-2999.

Figure 1: Normalized Si K-edge XANES spectra of (a) CaSiO_3 before use, (b) CaSiO_3 after use and (c) amorphous SiO_2 . Energy offset is taken to be 1835 eV.

Figure 2: Difference spectrum. $(b) - 0.5 \times (a) / 0.5$. (a), (b), see captions to Fig. 1.