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Development of Low-temperature Polarization-dependent Total Reflection Fluorescence XAFS (LT-PTRF-XAFS)

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1 Introduction

Metal-support interaction is an essential governing factor of the catalytic activity in heterogeneous catalysts. Unveiling the interaction, XAFS could be the most practical tool though it gives only one-dimensional information in general. To overcome the limitation, Polarization-dependent Total Reflection Fluorescence XAFS (PTRF-XAFS) has provided three-dimensional information which allows determining the metal-support interfacial bonds.[1] However, this state-of-art technique is still scope for improvement in S/N ratios, S/B ratios, and time resolution.

In the proposal (2016G551), we have challenged to improve the S/N ratios in the PTRF-XAFS spectra by employing a low-temperature measurement. Generally, temperature effects damp EXAFS amplitudes through the dynamic (thermal) disorders. Moreover, the effect relates to the S/N ratios in higher frequency EXAFS oscillations. A low-temperature measurement, therefore, has been applied as an effective solution. However, the crucial difficulty in isolating the mechanical vibration from a cryostat disturbs to obtain LT-PTRF-XAFS spectra.

In the report, we intorduce our recent progress suppressing the technical issue, and demonstrate the first low-temperature PTRF-XAFS (LT-PTRF-XAFS) results.

2 Experiment

To maintain a total reflection contion at low temperatures, we modified a liquid He-flow cryostat (STVP-100, JANIS, U.S.A.) which has no mechanical vibration while reducing the temperature. The modified cryostat was installed to a high precision 3-axis stage (Fig. 1). LT-PTRF-XAFS measurements were performed at the BL-9C of PF (2.5 GeV, 450 mA, Si(111)).

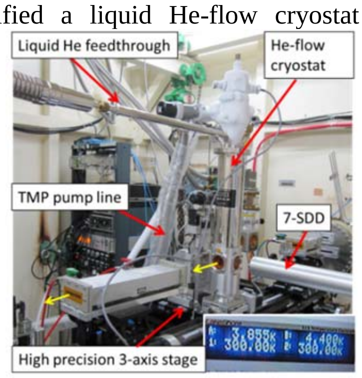


Fig.1 LT-PTRF-XAFS system.

Fluorescence signals were detected with 7-elements Silicon Drift Detector (XSDD50-07, Techno AP, Japan). XAFS measurements were carried out in the parallel orientation relative to the electric vector (***E***) of the incident X-rays. The Cu-HKUST-1 thin film on a single crystal Si(100) surface was prepared by a drop casting[2].

3 Results and Discussion

Fig. 2 (a) and (b) shows the $k^3\chi(k)$ LT-PTRF-EXAFS spectra of Cu-HKUST-1/Si(100) where ***E***// [100] surface. We found a fine shoulder in ~5 $Å^{-1}$. It suggests that the LT-PTRF-XAFS improves S/N ratios. Noteworthy is the XANES feature (Fig. 2(c)). The weak pre-edge (appeared at around 8985 eV) at RT becomes a sharp feature at 4 K. Moreover, we found that the feature was reversible. The pre-edge feature has assigned to the $1s \rightarrow 4p_{xy}$ dipolar shakedown transition which indicates the existence of Cu(II). We, therefore, assumed that the reversible feature would be related to the orientation of the ligands in Cu-HKUST-1.

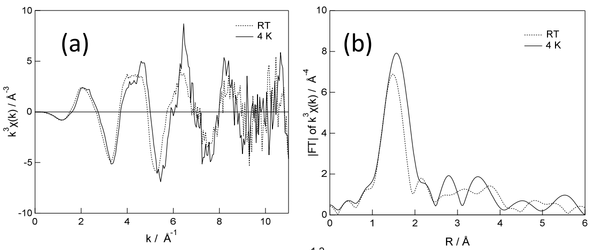
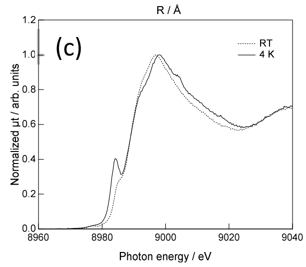


Fig. 2 Cu K-edge LT-PTRF-XAFS of Cu-HKUST-1/Si(100) (a) $k^3\chi(k)$ spectra, (b) FT results ($k = 3\sim11Å^{-1}$), (c) XANES spectra.



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References

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