

Identification of Tars from the Viewpoint of Graphitic Structures by using Soft X-Ray Absorption Spectroscopy

1. Introduction: Tar is important industrial carbon materials which are used for sources of various functional carbon materials and for weather-proof coating materials. Tar is carbonized product from coal, petroleum, and woods. Hence, tar is generally complicated mixture of various organic compounds. Aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons (PAHs), are main component of tar. Such the organic components in tar are usually analyzed by using chromatographic methods. However, other useful analytical methods, which can enable to identify the graphitic structures in tar, have been recently required in tar industry.

Soft X-ray absorption spectroscopy (XAS) has been a powerful analytical tool for carbon materials. To identify tars by using the XAS method, we have measured X-ray absorption near-edge structure (XANES) in CK, NK, and OK regions of tar samples in this study.

2. Experiments: Six tar samples labelled as T1 ~T6 were supplied from a chemical company in Japan. The tar samples were diluted with organic solvent, and coated on Au substrates. Highly oriented pyrolytic graphite (HOPG) and carbon black (CB) N660 were used as references. XAS and XANES spectra of the tar samples were measured in BL-6.3.2/ALS [1] and BL10/NewSUBARU [2] by using a total-electron-yield (TEY) method.

3. Results and Discussion: Figure 1 shows XAS spectra in the 200 ~ 600 eV region of T1~T6 samples. CK peaks were dominantly observed in the samples. This confirms that main component of tar is hydrocarbons. On the other hand, NK and OK peaks were slightly observed, which suggests nitrogen and oxygen are partially incorporated with the main hydrocarbons. It is confirmed from finger-print analyses of NK- and OK-XANES that nitrogen takes $-NH_2$, $>NH$, $>N-$, and $=N-$ forms, and oxygen takes mainly $C=O$ form.

Figure 2 (a) shows the CK-XANES of T1~T6 with the reference HOPG and CB. Comparing to HOPG, tar samples exhibit broader π^* peak profiles which are similar to CB. Such the broad π^* peak profile suggests the edge carbon atoms in graphitic structures [3,4]. To analyze the graphitic structure of tar samples, broader portion of the π^* peak can be obtained from the

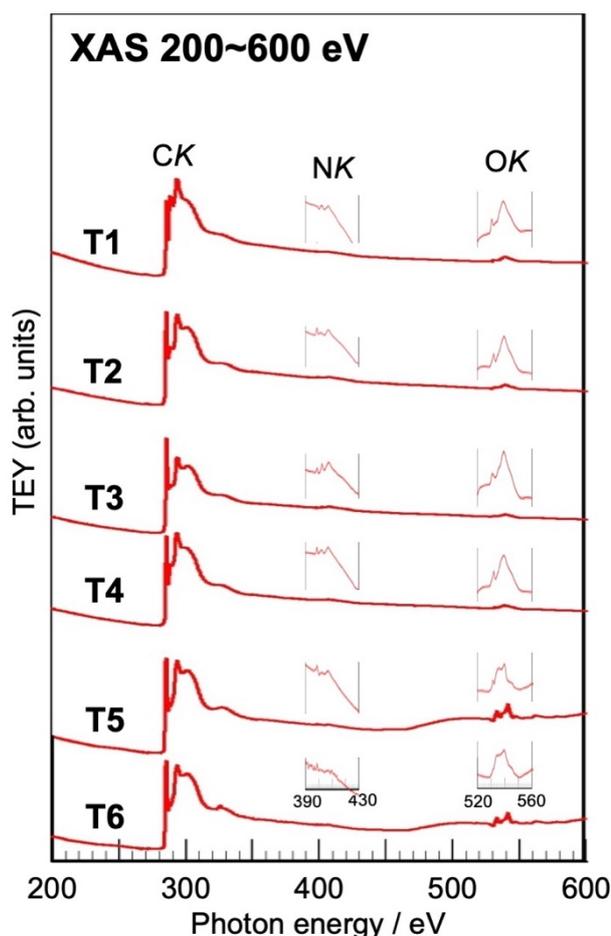


Figure 1 TEY-XAS of the tar samples (T1~T6). Enlarged spectra in the NK and OK regions are shown on the individual spectrum.

subtraction of the CK-XANES between tar samples and HOPG. The broader portion in lower energy side can be shown as a small peak denoted as *a*. Thus, peak *a* height means the broader index of π^* peak compared to HOPG. Relationship between the peak *a* height and π^* peak height, which has been named as " π^* peak map" [5], of tar sample is shown in Figure 2(b). In the π^* peak map, distributions of nano-graphite and various CB [5] are shown as references. T1 distributes on the region of CB and nano-graphite. However, other tar samples distribute upper region of them. This means that T1 takes similar amorphous graphitic structure of CB, and other tar samples take smaller graphitic structures such as PAHs. It is especially suggested that T3 takes smaller PAH molecules than other tar samples.

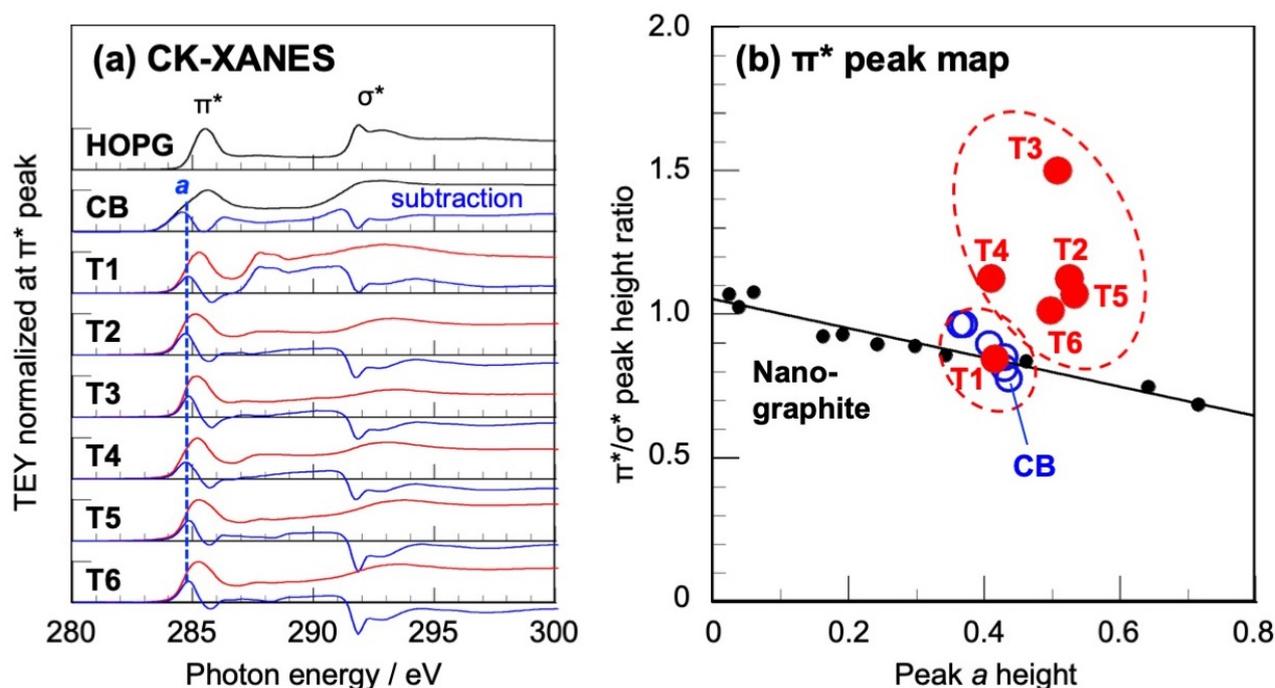


Figure 2 Left panel (a) shows the CK-XANES of the tar samples (T1~T6) and reference samples (HOPG, CB). Right panel (b) is the π^* peak map of the tar samples with CB and nano-graphite as references.

4. Conclusion: To identify tars from the viewpoint of graphitic structure, soft X-ray absorption spectra of tars were measured. Small portion of nitrogen and oxygen in tars can be successfully detected by the TEY method. From CK-XANES and the π^* peak map, tars can be identified from the viewpoint of graphitic structure. Graphitic size of tar distributes from small PAHs to larger CB. It is concluded that soft X-ray absorption spectroscopy and the π^* peak map are useful to identify tars.

References

- [1] J. H. Underwood, E. M. Gullikson, M. Koike, P. J. Batson, P. E. Denham, K. D. Franck, R. E. Tackaberry, and W. F. Steele, *Rev. Sci. Instrum.* 67 (1996) 3372.
- [2] Y. Muramatsu, A. Tsueda, T. Uemura, T. Harada, and H. Kinoshita, *Adv. X-Ray Chem. Anal. Japan*, 44 (2013) 243-251.
- [3] Y. Muramatsu, R. Harada, and E. M. Gullikson, *Proceedings of the X-ray Absorption Fine Structure-XAFS13 (2007)* 511-513.
- [4] Y. Muramatsu, T. Ooe, T. Okada, and E. M. Gullikson, *Proceedings of the 9th International Symposium on Atomic Level Characterizations for New Materials and Devices '13, ALC'13 (2013)* 516-518.
- [5] Y. Muramatsu, K. Murayama, and T. Okada, *Proceedings of the 10th International Symposium on Atomic Level Characterizations for New Materials and Devices '15, ALC'15 (2015)* 27p-P-38.