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AN ANALYSIS OF CHEMICAL STRUCTURE OF CARBON EDGE SITES BY USING DEUTERIUM-LABELING TEMPERATURE-PROGRAMMED DESORPTION TECHNIQUE

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Introduction

Temperature programmed desorption (TPD) technique is used to characterize and quantify oxygen-containing functional groups formed on the edge sites of carbon materials. There is a problem that TPD can not distinguish phenolic group (-OH) and ether (-O-) because both of these functional groups are decomposed as CO at around 600 to 700 °C. The thermal decomposition behaviors of phenol and ether caused in the TPD run are not completely consistent. Since phenolic group contains hydrogen atom in its chemical structure, as shown in **Figure 1**, it is considered that H_2 is desorbed by further increasing the temperature after emitting CO. By labeling the hydrogen atom in a phenolic group with deuterium, it is considered that hydrogen derived from phenolic group can be detected separately as deuterium in TPD measurement. Therefore, the deuterium-labeling TPD technique makes it possible to distinguish phenolic group and ether by observing the desorption of deuterium species. In this study, we propose an accurate analysis method for surface functional groups formed on carbon edge sites by using deuterium-labeling TPD technique that can distinguish phenolic group and ether, and aim to verify its validity.

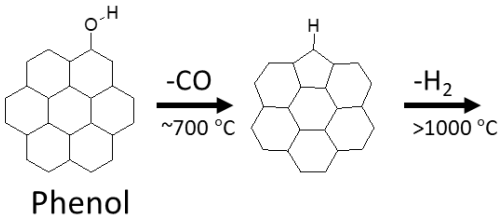

Figure 1. Schematic images of thermal decomposition of phenolic group.

Materials and Methods

Activated carbon (MSC30, Kansai Coke & Chemicals Co., Ltd.) was used as a sample. The sample was placed in a sealable vial and vacuum dried in the vial. With the vial sealed under vacuum, D_2O was introduced into the vial using a syringe to prepare a suspension of D_2O/sample. The suspension was heated to 60 °C and maintained for 24 h in order to accelerate the proton exchange reaction of the oxygen-containing functional group. The suspension was placed on a sample holder and lyophilized in a TPD apparatus (details of the apparatus are described in our previous study [1]), and then subjected to TPD measurement.

Results and Discussion

Figure 2 shows the TPD spectrum of deuterium-labeled MSC30. Although the desorption of D_2O, DHO, D_2, and DH was confirmed, that of H_2O was not observed. The total amount of desorption of deuterium determined from TPD agreed with the amount of acidic functional groups determined by Boehm method [2]. This indicates that hydrogen atoms of carboxylic and phenolic groups are

deuterium-substituted by D_2O. Furthermore, it is considered that D_2O observed in the TPD spectra has no contribution from adsorbed water. In order to investigate the oxygen-containing functional group with the TPD spectra, it is necessary to consider the desorption mechanisms of the deuterium species. The mechanisms are divided into cases according to the functional groups and its surrounding chemical structure. For example, in the case of phenolic group, desorption species differ according to the surrounding chemical structure of it, as shown in **Figure 3**. D_2O is formed if carboxylic are adjacent, and DHO if hydrogen are adjacent. In the absence of their adjacent functional groups, D_2/DH is desorbed after CO desorption. Thus, deuterium labeled TPD can provide information not only on the type of functional group but also on the chemical structure around the functional group. In this study, it was assumed that 12 kinds of chemical structures shown in **Figure 4a** exist in the carbon edge sites. These chemical structures follow different thermal decomposition processes. **Figure 4b** shows the results of quantification of the chemical structures of MSC30. Deuterium-labeled TPD technique allows us to distinguish and quantify phenolic group and ether, and furthermore, functional groups can be classified according to the chemical structure around the functional groups.

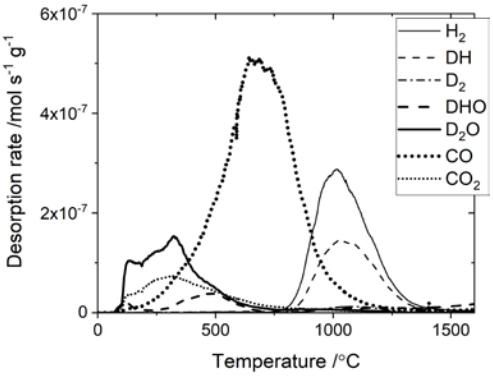

Figure 2. TPD spectrum of deuterium labeled MSC30.

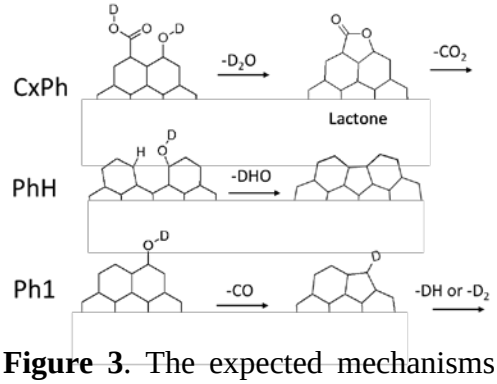

Figure 3. The expected mechanisms of D_2O, DHO, DH and D_2 formation reactions.

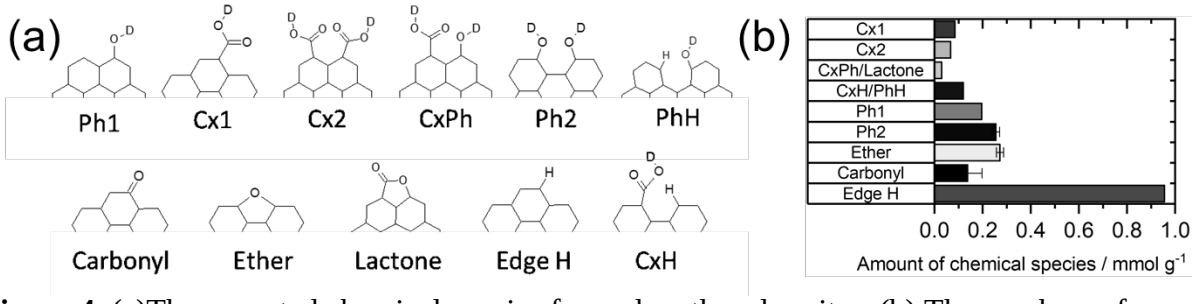

Figure 4. (a)The expected chemical species formed on the edge sites. (b) The numbers of chemical species formed in MSC30.

References

1. T. Ishii, S. Kashihara, Y. Hoshikawa, J. Ozaki, N. Kannari, K. Takai, T. Enoki and T. Kyotani, *Carbon*, 2014, **80**, 135-145.

2. Y.S. Kim and C.R. Park, Ed. M. Inagaki and F. Kang, Materials Science and Engineering of Carbon: Characterization, 2016, Elsevier Inc.