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In situ QXAFS Analysis for Hydrodeoxygenation of a Bio-oil Model Compound on Ni_2P/MCM-41

Gwang-Nam Yun[1], So-Jin Ahn[1], Atsushi Takagaki[1*], Kyoko K. Bando[2], and S. Ted Oyama[1*]
[1]The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[2]National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, 305-8565, Japan

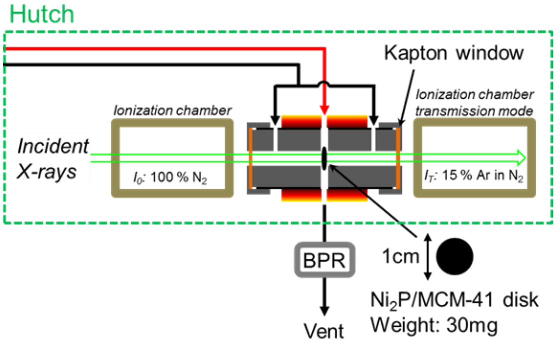
1 Introduction

Bio-oil derived from biomass is being considered as a sustainable source for the production of a variety of chemicals and fuels [1]. A major barrier in the application of the bio-oil is that it contains large levels of oxygen containing compounds (35 ~ 40 wt. %) which result in low heating value and chemical instability [2, 3]. Hydrodeoxygenation (HDO) is a key process to lower the oxygen content of biomass streams. Here we report in situ QXAFS analysis for hydrodeoxygenation of γ-valerolactone (GVL) on Ni_2P/MCM-41 to prove the working state of Ni site during reaction.

2 Experiment

In situ QXAFS at the Ni K edge (8.333 keV) of the Ni_2P/MCM-41 was recorded in the energy range 8.233-9.300 keV using the bending magnet beam line 9C of Photon Factory (PF). About 30 mg of Ni_2P/MCM-41 was pressed into a disk with diameter of 10 mm and set in the in situ cell. The catalyst was reduced at 550 °C under hydrogen flow (50ml/min) and then reactant (GVL) was introduced into the cell by bubbler at 0.5 MPa. For temperature-dependence tests, after the pretreatment, the catalyst was stabilized for 20 min and then the gas mixture (4 mol % GVL in H_2) was introduced into the cell at the reaction temperature and a pressure of 0.5 MPa. The measurement was repeated at 350, 300, and 250 °C with each temperature maintained for 80 min to reach steady-state conditions. After each measurement, the catalysts were treated at 550 °C for 3 h in H_2 flow.

The X-ray absorption spectra were recorded in transmission mode using ionization chambers for the detection of primary (I_0, 100 % N_2) and transmitted (I_T, 15% Ar balanced with N_2) beam intensities.



Scheme 1. In situ quick x-ray absorption fine structure (QXAFS) reactor system

3 Results and Discussion

Figure 1 shows the transient XANES signal at 8347 eV before and after GVL injection at 250, 300, and 350 °C and 0.5 MPa under H_2 with 4 mol% γ-GVL. The signal is normalized to the edge-jump, and a zero absorption in the reduced state. The change of absorbance at 8347 eV was used to track the state of the Ni species. Under H_2 flow, the signals were stable at all temperatures indicating that Ni was in the same initial reduced state. At 250 °C, the changes in absorbance were very small, while at higher temperature, significant changes in absorbance were observed with the absorbance increasing as temperature was increased. This suggests that at higher temperature the adsorption and transformation of GVL to intermediates on Ni sites were enhanced, resulting in the formation of Ni^+ on the surface

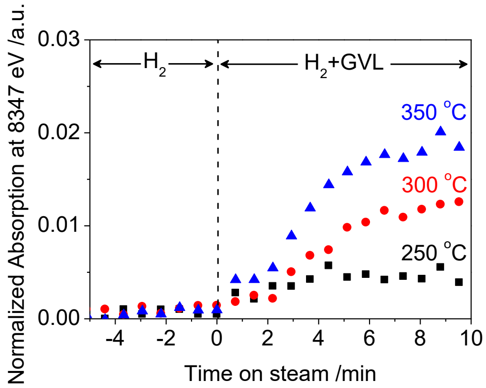


Figure 1. Transient XANES signal at 8347 eV before and after GVL injection at 250, 300, and 350 °C and 0.5 MPa under H_2 with 4 mol% GVL

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* ted_oyama@chemsys.t.u-tokyo.ac.jp