

In situ QXAFS Analysis for Hydrodeoxygenation of a Bio-oil Model Compound on Ni₂P/MCM-41

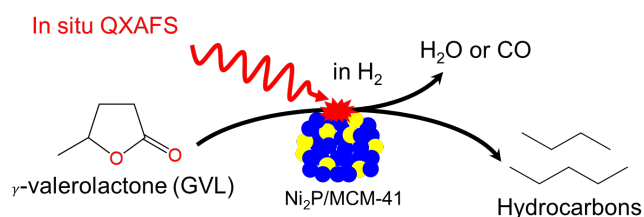
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1 Introduction

Bio-oil is one of the promising energy sources due to renewable and a rich source of carbon and has become of considerable interest owing to possibility of development as an alternative fuel. However, the bio-oil cannot be directly used as a fuel because it has high oxygen content which leads to low heating value, high viscosity, low pH, incompatibility with conventional fuels, and chemical instability. Hydrodeoxygenation is needed to improve the bio-oil properties being eliminating oxygen molecule in bio-oil. Here we report in situ QXAFS analysis for hydrodeoxygenation of gamma-valerolactone on Ni₂P/MCM-41 as shown in Scheme 1.



2 Experiment

In situ QXAFS at the Ni K edge (8.333 keV) of the Ni₂P/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 40 mg of Ni₂P/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. The reaction temperature was varied downward and upward in the order: 350, 300, 250, 275, and 325 °C with each temperature maintained for 1 h. The X-ray absorption spectra were recorded in transmission mode using ionization chambers for the detection of primary (I₀, 100 % N₂) and transmitted (I_t, 25% Ar balanced with N₂) beam intensities. Catalytic activity test was carried out in a continuous-flow reactor operated at 0.5 MPa and reaction conditions were similar with those in situ QXAFS measurement.

3 Results and Discussion

Figure 1 shows normalized XANES spectra during the hydrodeoxygenation of GVL at 250 – 350 °C and 0.5 MPa of H₂. Absorbance at white line around 8350 eV increased with increasing reaction temperature. This indicates that during the reaction oxidation state of Ni sites on the catalyst increased due to chemical adsorption of GVL on

Ni sites [1,2]. The dependency of the absorbance at white line on reaction temperature was in good agreement with that of catalytic activity as shown in Figure 2. It is considered that more GVL or intermediates could be adsorbed on Ni sites on the catalyst at high temperature, resulting in increase of the absorbance at white line.

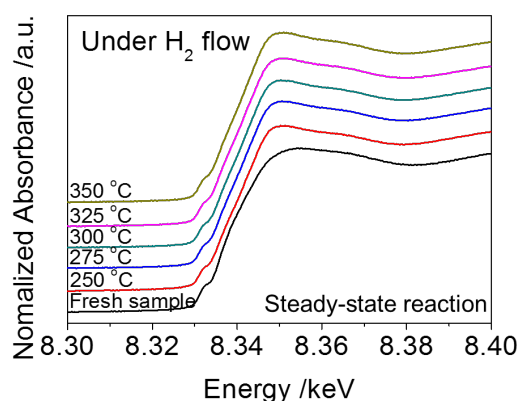


Figure 2 Normalized XANES spectra at 250–350°C

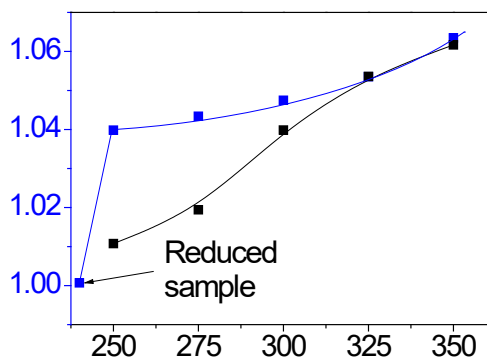


Figure 3 Normalized absorbance at white line and GVL conversion as a function of temperature

References

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