

## In situ QXAFS Analysis for Hydrodeoxygenation of $\gamma$ -Valerolactone on MCM-41-supported Ni<sub>2</sub>P Catalyst

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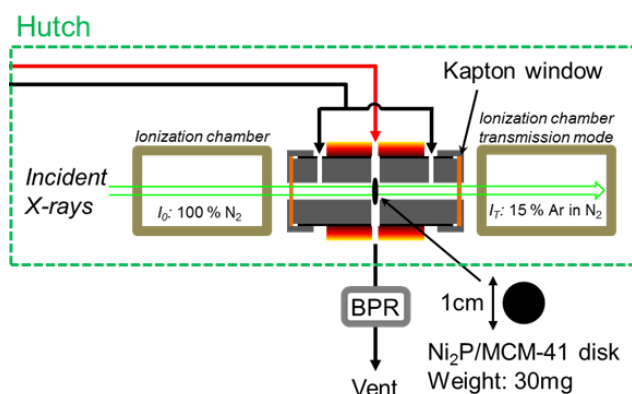
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### 1 Introduction

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 consists contains large levels of oxygen containing compounds (35 ~ 40 wt. %) which result in low heating value and chemical instability [2]. Hydrodeoxygenation (HDO) is a key process to lower the oxygen content of biomass streams. Here we report in situ QXAFS analysis for hydrodeoxygenation of gamma-valerolactone on Ni<sub>2</sub>P/MCM-41.

### 2 Experiment

In situ QXAFS at the Ni K edge (8.333 keV) of the Ni<sub>2</sub>P/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 Ni<sub>2</sub>P/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 the effect of GVL partial pressure, after the pretreatment, the catalysts were stabilized at 300 °C and 0.5 MPa for 20 min. The GVL partial pressure was varied in the order: 20, 16, 8, 2, 4 and 12 kPa by adding H<sub>2</sub> as a diluent after the bubbler to maintain a constant total flow rate (50 ml/min). The X-ray absorption spectra were recorded in transmission mode using ionization chambers for the detection of primary ( $I_0$ , 100 % N<sub>2</sub>) and transmitted ( $I_T$ , 25% Ar balanced with N<sub>2</sub>) 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 in effect of GVL partial pressure at 300 °C and 0.5 MPa in H<sub>2</sub>. After introduction of GVL, absorbance at white line around 8350 eV significantly increased. Furthermore, with increasing reaction temperature the absorbance gradually increased. This absorbance is due to Ni<sup>δ+</sup> which can be related with adsorbates. Therefore, the increase of absorbance at white line is because of absorption of GVL and intermediate species (Figure 2). Again, with increasing GVL partial pressure, more GVL can be absorbed on more Ni sites.

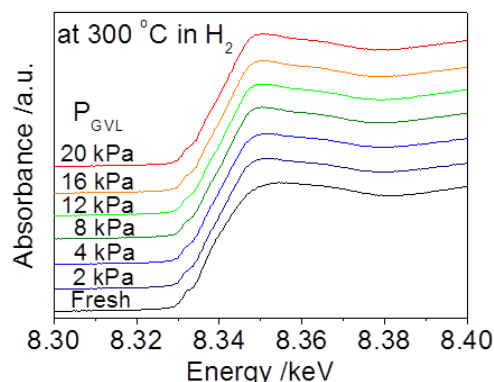


Figure 1 Normalized XANES spectra (effect of GVL partial pressure at 300°C and 0.5 MPa)

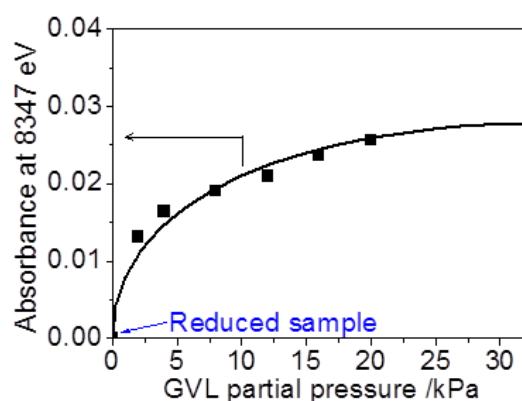


Figure 2 Normalized absorbance at white line at 300°C and 0.5 MPa

### References

- [1] G.S. Foo, A.K. Rogers, M.M. Yung and C. Sievers, *ACS Catal.*, **6**, 1292 (2016).
- [2] H. Wang, J. Male and Y. Wang, *ACS Catal.*, **3**, 1047 (2013).

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