Structural studies on Ni phosphide catalysts by Operando XAFS

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1 Introduction

The thermal treatment of biomass yields a liquid product that is known as biooil, which is a promising substitute for petroleum derived fuels, but which contains high levels of oxygen which reduce the heating value and make the oil unstable [1]. The purpose of this study is to investigate a new catalyst for oxygen removal, nickel phosphide. These materials were shown to have high activity in sulfur and nitrogen removal, so are promising candidates. As a model for biooil, use is made of the compound 2-methyltetrahydrofuran (2MTHF).

2 Experiment

The Ni₂P/SiO₂ catalyst was prepared by a temperature-programed reduction method from supported phosphate precursors. Reactivity studies were carried out in a flow reactor at 0.4 MPa using a mixture of 95 vol% of 2-MTHF and 5 vol% of n-heptane as an internal standard mixed with a H₂ gas to give a reactant stream of 3 or 5 mol% 2-MTHF in H₂. X-ray absorption spectra at the Ni K-edge of reference and catalyst samples were recorded in the energy range 8.233 keV. Measurements were carried out by standard transmission mode using a Si (111) monochrometer double crystal at room temperature on BL7C beam line at KEK-PF and BL14B2 at SPring-8.

3 Results and Discussion

The reactivity of the Ni₂P/SiO₂ is shown in Fig.1. The results show that the major products were the deoxygenated products n-pentane and n-butane. As intermediates, 2-pentanone, 2-pentanol and 1-pentanol were observed. These suggest that the HDO proceeds as shown in Fig 2.

Fig. 3 shows the Fourier transformed Ni K-edge EXAFS spectra for Ni₂P/SiO₂ and bulk Ni₂P. The peak which corresponds to Ni-Ni bond was weakened in the Ni₂P/SiO₂, indicating that small particles of Ni₂P were formed on silica. Each parameter in Ni₂P/SiO₂ was as follows. Ni-P (CN:2.0, R: 2.22Å, σ²: 0.0024 Å²); Ni-Ni (CN: 2.6, R: 2.66Å, σ²: 0.0092 Å²).

References


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Fig. 1: Contact time study of 2-MTHF HDO over Ni₂P/SiO₂.

Fig. 2: A proposed reaction network for 2-MTHF HDO.

Fig. 3: Fourier transformed Ni K-edge EXAFS for bulk Ni₂P and Ni₂P/SiO₂.