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Structural studies on Ni phosphide catalysts by Operando XAFS

Atsushi Takagaki[1], Ara Cho[1], S. Ted Oyama[1,2,*], and Kiyotaka Asakura[3,*]
[1]School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan
[2]Virginia Polytech Institute and State University, Blacksburg, Virginia 24061-0211, USA
[3]Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

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 Ni_2P/SiO_2 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 H_2 gas to give a reactant stream of 3 or 5 mol% 2-MTHF in H_2. 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 Ni_2P/SiO_2 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 Ni_2P/SiO_2 and bulk Ni_2P. The peak which corresponds to Ni-Ni bond was weakened in the Ni_2P/SiO_2, indicating that small particles of Ni_2P were formed on silica. Each parameter in Ni_2P/SiO_2 was as follows. Ni-P (CN:2.0, R: 2.22Å, σ^2: 0.0024 Å^2); Ni-Ni (CN: 2.6, R: 2.66Å, σ^2: 0.0092 Å^2).

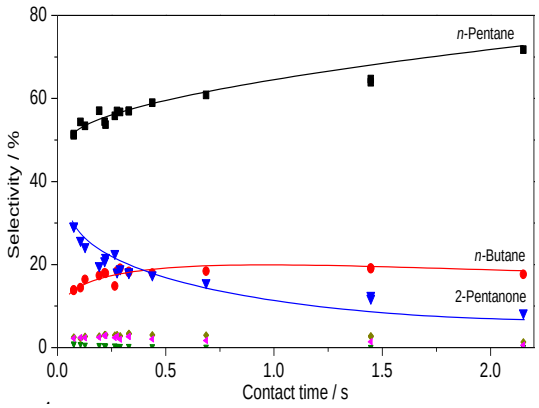

Fig. 1: Contact time study of 2-MTHF HDO over Ni_2P/SiO_2.

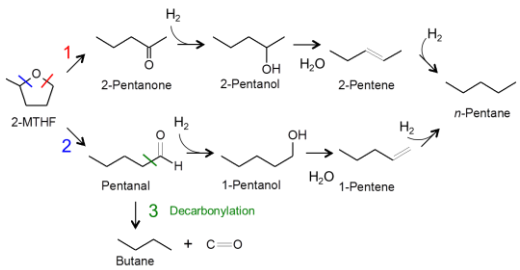

Fig. 2: A proposed reaction network for 2-MTHF HDO

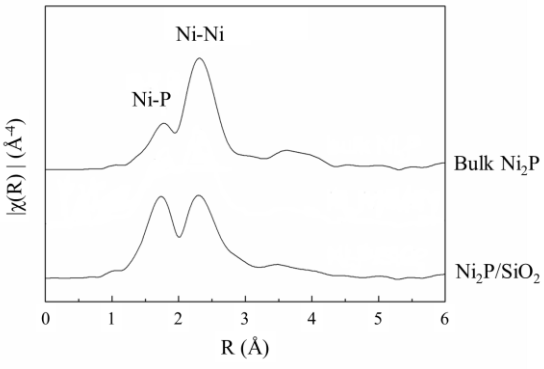

Fig. 3: Fourier transformed Ni K-edge EXAFS for bulk Ni_2P and Ni_2P/SiO_2.

References

[1] A.V. Bridgwater, Biomass & Bioenergy **38** (2012) 68-94.

* ted_oyama@chemsys.t.u-tokyo.ac.jp; askr@cat.hokudai.ac.jp