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Study of Ni_2P Activation using in situ Quick XAFS

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Introduction

The removal of sulfur and nitrogen from petroleum feedstock is a very important process because of strict global regulations to limit the sulfur content in fuel and requirements to clean up exhaust gases. Nickel phosphide Ni_2P has been reported as a new catalyst with high activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Since Ni_2P is oxidized by passivation, a reduction is required before HDS and HDN reactions, which is called activation. Ni_2P is known to be able to recover from the oxidized state by temperature program reduction (TPR) up to 773 K. However, the details of the activation have not been clear. Because the ramping rate was 5 K/min, it was difficult to measure EXAFS, which takes >5 min/scan. We studied the details of the activation using Quick XAFS (QXAFS), which can measure one Ni K-edge EXAFS within 8 seconds.

Experimental

The in situ QXAFS spectra were measured by transmission mode at NW10A. The sample was pressed into a pellet and then set in a controlled-atmosphere cell. The sample was heated to 773 K at 5 K/min and kept 2 h under pure hydrogen flow (50 sccm). The gas products from the cell were monitored simultaneously using an IR gas detector. The XAFS spectra were measured from 8143.52 eV to 8983.24 eV, which is correspond to k ~ 130 nm^{-1}. The XAFS data were recorded during as the monochromatar was scanned from low to high energy. Each XAFS spectrum took 8 s to measure.

Results and Discussions

Figure 1 shows the production of water recorded by an IR detector during TPR. Two water production peaks were observed. It shows that the activation took place in three stages as shown in Fig.1. Figure 2 shows the Fourier Transforms of the k^3-weighted EXAFS spectra. Two FT peaks at ca. 0.18 and ca. 0.29 nm were observed before activation (t = 0 s). Curve fitting analysis revealed that the first peak corresponded to Ni-O bonds of ca. 0.204 nm length and the other one corresponded to Ni-Ni bonds of ca. 0.310 nm length, which because the structure was similar to that of $Ni(OH)_2$, suggested that the Ni_2P before activation was oxidized. The position and shape of the first peak did not change in stages I and II, which suggested that the Ni was still oxidized and the first neighbor of a Ni atom were oxygen. The second peak became weak in stage I and disappeared in stage II. These results indicated that in stage I, $Ni(OH)_2$-like particles converted to small NiO clusters by the release of weakly interacting oxygen. In stage III, the first peak started to shift to longer distance and a shoulder peak began to grow and water production also started, which indicated that Ni was being reduced and Ni_2P started to form.

The in situ QXAFS with simultaneous monitoring of gas production revealed that the activation of Ni_2P catalyst took place in three stages.

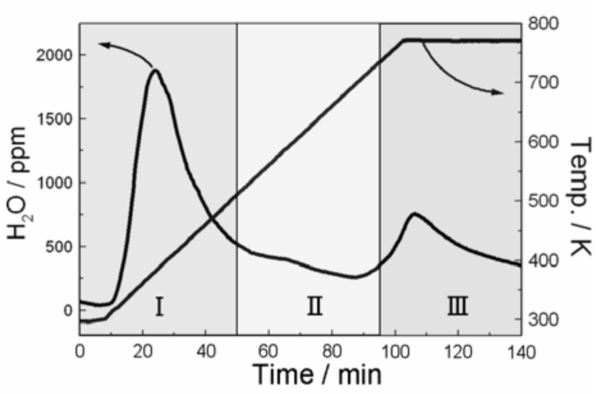

Figure 1: The amount of water in the gas products during activation process

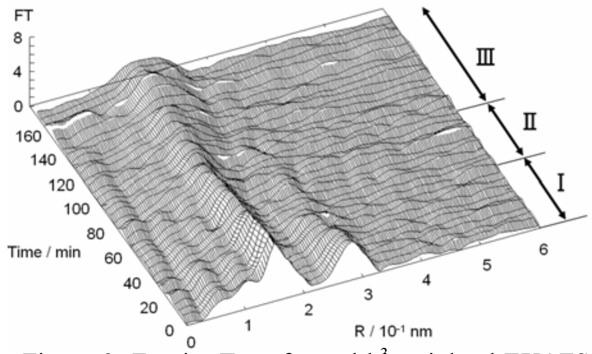

Figure 2: Fourier Transformed k^3-weighted EXAFS spectra during activation process

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