

Structural studies on Ni phosphide catalysts by Operando XAFS

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Introduction

Supported nickel phosphides (Ni₂P) catalysts, which show an outstanding capabilities in the hydrotreating of petroleum feed stocks [1], are considered as promising catalysts in the hydrodeoxygenation (HDO) reaction of biomass-derived oil. Especially, Ni₂P supported on K-ion exchanged USY (Ni₂P/KUSY) catalysts showed to have higher activity than a commercial NiMoS for the hydrodesulfurization (HDS) of model oils[2].

This study is focused on understanding of the Ni₂P/KUSY structure and of relationship between structural properties and HDO reaction mechanisms.

Experimental

Ni₂P catalysts were prepared with KUSY and silica as supporting materials by incipient wetness impregnation method. Details are described elsewhere [2]. Desired amount of sample, which was calculated with a program SAMPLEM4M, was pelletized and reduced in the quartz reactor. Reduced samples were transferred into the glove box without exposure to air and sealed.

Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra were collected in a transmission mode using a Si (111) monochromator double crystal at room temperature on BL9C beam line. EXAFS data from individual samples were Fourier transformed in the range from 3 to 14 Å⁻¹ and data processing was performed using program WinXAS97.

Results and Discussion

Figure 1 shows the Fourier transformed Ni K-edge EXAFS spectra of various Ni₂P samples and Table 1 summarizes the EXAFS parameters which were obtained as a result of curve-fitting[3]. In Figure 1, the first peak appeared at around 1.7 Å corresponds to a Ni-P (I) bond whose coordination number is almost 2 in both cases as was found in reference. The second peak appeared at around 2.3 Å corresponds to Ni-Ni bonds. This peak was weakened in the supported catalysts, which means small size of the particles [3]. Highly dispersed Ni₂P/KUSY catalyst may induce high activity in HDO reaction which requires hydrogenation activity.

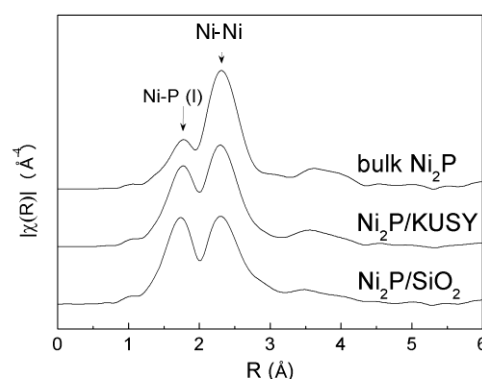


Figure 1. Fourier transformed Ni K-edge EXAFS of the Bulk Ni₂P, Ni₂P/KUSY and Ni₂P/SiO₂.

Table 1: EXAFS parameters for Ni₂P/KUSY and Ni₂P/SiO₂

	Ni-P(I)	Ni-Ni
Reference		
CN	2	4
R/Å	2.27	2.68
Ni ₂ P/KUSY		
CN	2.1	2.4
R/Å	2.23	2.64
σ ² /Å ²	0.0008	0.0081
Ni ₂ P/SiO ₂		
CN	2.0	2.6
R/Å	2.22	2.66
σ ² /Å ²	0.0024	0.0092

References

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