Chemistry

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# QXAFS studies on the structure of $Ni_2P$ in MCM-41 during reaction conditions

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## Introduction

$Ni_2P$ is a new class of dehydrogenation catalysts. When it is supported on MCM-41, a high surface area support, it shows a quite high activity. We conducted the in-situ XAFS studies during the hydrodesulfurization reaction. We found two kinds of structure change depending on the conditions.

## Experimental

All XAFS experiments were carried out at BL9C and NW10A beam lines, using Si(111) and Si(311) monochromators, respectively. $Ni_2P$ /MCM 41 was loaded into an in-situ cell and reduced at 873 K under the flow of $H_2$. We followed the structure change of thiophene dehydrogenation reaction under the presence and absence of hydrogen.

## Results and Discussion.

Figure 1 shows the difference spectra before and after the thiophene hydrodesulfurization reactions.

There were clear oscillations in the difference spectra for each reaction temperature. The topmost oscillation indicated the FEFF-calculated one assuming the Ni-S distance at 0.227 nm and coordination number with 0.1. There was a complex temperature dependence in the amplitude. At 240ºC, a large oscillation appeared. It decreased at 280ºC but gradually increased with temperatures again. The creation of Ni-S bond may depend on the reaction conditions. At low temperature, the overall reaction does not smoothly proceeded so that the surface S was accumulated. By increasing the temperature, the hydrogen dissociation on this surface was accelerated and the surface S was removed by the dissociated hydrogen. However, at higher temperature, the amount of adsorbed hydrogen became lower because of the adsorption-desorption equilibrium while decomposition reaction constantly increased. Finally the S was accumulated.

On the other hand when the $Ni_2P$ was exposed to thiophene we found another type of adsorbed species. Figure 2 shows the difference spectra before and after the exposure to thipohene at various temperatures. The amplitude of the oscillation monotonically decreased with the temperature increase though there was again clear appearance of sinusoidal oscillations. FEFF shows the different bond length compared to the oscillation appearing in the difference spectra of the sample under thiophene+$H_2$ flow. Ni-S bond was found at 0.240 nm. Because the oscillation decreased monotonically with the temperature, the Ni-S bond in this case was due to the thiophene adsorption on the $Ni_2P$ surface. The work indicated that the thiophene decomposition requires the hydrogen.

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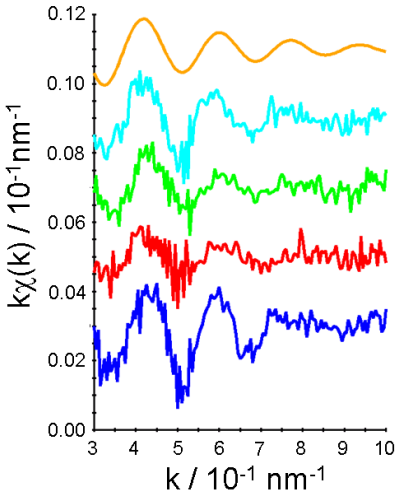


Figure 1 difference spectra of $Ni_2P$ XAFS before and after the reaction with thiophene + $H_2$. From top to bottom,FEFF simulation, 400ºC, 320ºC, 280ºC, 240ºC,

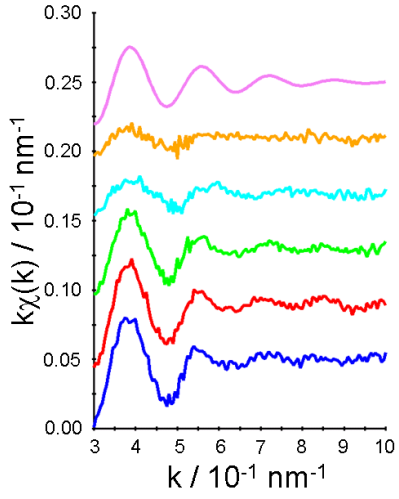


Figure 2 difference spectra of $Ni_2P$ XAFS before and after the adsorption of thiophene. From top to bottom,FEFF simulation, 400ºC, 320ºC, 280ºC, 240ºC,