Chemistry

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A New High Pressure and High Temperature Cell for an Operando EXAFS Observation of Hydrodesulfurization Catalysts

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Introduction

The hydrodesulfurization catalysts are important in order to decrease sulfur compounds in fuels, which are the source of SO_x and the acid rain. In order to develop high performance hydrodesulfurization catalysts, operando structure analysis is indispensable. EXAFS is the best tool for this purpose. However, operando EXAFS studies on the hydrodesulfurization catalysts are quite difficult because of the presence of high pressure and high temperature oils, which absorb X-ray strongly. We have constructed a new cell which enables us to carry out the operando EXAFS of Ni_2P catalysts (the most active hydrodesulfurization catalysts) in the presence of 3 MPa liquid hydrocarbons at 600 K.

Experimental

A new cell design

Figure 1 shows a new cell for measurement of EXAFS under high pressure and high temperature liquid phase reaction conditions. The window material we used in this work is high purity binderless c-BN (Sumitomo Electric Industries, Ltd) It is the hardest material second to diamond. It is stable, non-toxic and does not give any diffraction peaks unlike Be or diamond.

Reaction conditions

We used the model oil containing 20 wt% tetralin and 77 wt% tetradecane with 3 wt% DBT (Dibenzothiophene). It was supplied to the catalyst with 3 MPa H2. The oil feed speed was 2 g / hour. The cell was heated up to 613 K and we measured EXAFS spectra under these high pressure and high temperature conditions.

Results and discussion

Figure 2 shows the EXAFS oscillations before the reaction and under the steady state operating conditions. Three spectra were quite similar to one another. As far as the authors know, this is the first operando EXAFS spectra for hydrotreating catalysts under the real catalytic conditions in the presence of oil at 3 MPa. We could find little difference between the two EXAFS spectra under hydrodesulfurization conditions. High-pressure operando EXAFS demonstrated that the Ni2P structure on SiO_2 was quite stable under the reaction conditions. In conclusion, Ni2P structure was stable even under the high-pressure reaction conditions.

In this work we carried out operando XAFS studies on Ni2P catalysts and the current system is supposed to be applicable to the operando EXAFS studies for other hydrotreating catalysts such as NiMoS, CoMoS and PtPd.

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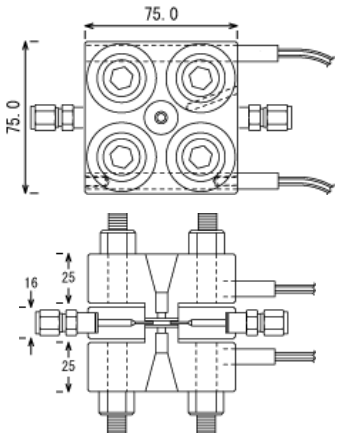

Figure 1 Diagram of the new high pressure and high temperature cell

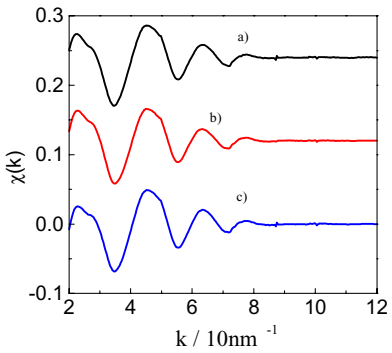

Figure 2 XAFS oscillations: (a) before reaction, (b) 9 hours after the reaction initiation, (c) 24 hours after the reaction initiation

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