

In situ Studies on the Activation Process of Ni₂P/ K-USY – Time Resolved QXAFS Combined with Gas Analysis –

Ni₂P/K-USY (K-promoted ultra-stable Y-type zeolite) is an efficient catalyst for hydrodesulfurization (HDS) of petroleum feedstocks. In this work, time resolved in situ quick X-ray absorption fine structure spectroscopy combined with on-line gas analysis was employed to follow the structural changes during the activation process of Ni₂P/K-USY. The activation was conducted on passivated samples by temperature programmed reduction from ambient temperature to 773 K under a flow of H₂. There were three phases in the transformation from the passivated state (Ni(OH)₂) to the final Ni₂P structure. The formation of atomically dispersed Ni²⁺ in Phase I was found to be crucial for the selective regeneration of Ni₂P.

Recently, Ni₂P has been recognized as an efficient catalyst for hydrodesulfurization (HDS) of petroleum feedstocks. Ni₂P/K-USY (K-promoted ultra-stable Y-type zeolite, surface area 784 m²/g) shows the highest level of performance because of the presence of fine Ni₂P particles as small as 1.1 nm in diameter. When the catalyst is used for reaction, it is activated by temperature programmed reduction (TPR) to regenerate an active Ni₂P structure, because the catalyst undergoes passivation (under 0.5% O₂/He at room temperature) after the synthesis. In spite of the importance of the activation process, little is known about structural transformation during activation.

QXAFS (Quick X-ray Absorption Fine Structure) spectroscopy is a technique that can be used to obtain a XAFS spectrum in less than one minute. With this system, a time resolution of 30 s is realized for Ni K-edge XAFS measurements. In the present study, on-line gas analysis was employed together with QXAFS. Structural changes during activation are discussed in connection with gas phase analysis, which provides a precise determination of the transformations, and reveals a key factor which controls the formation of active species.

For XAFS analysis, passivated Ni₂P/K-USY was pressed into a pellet and set in an in situ XAFS cell. Activation by TPR was carried out from room temperature

to 773 K at 5 K/min and then the sample was kept at 773 K for 2 h under a flow of H₂ of 50 cm³/min. The effluent gas was monitored with an IR gas analyzer (MKS Multigas 2030). In situ QXAFS was carried out at AR-NW10A in transmittance mode [1].

Ni K-edge EXAFS (Extended X-ray Absorption Fine Structure) analysis shows that the structure of Ni species in passivated Ni₂P/K-USY is Ni(OH)₂, and that it turns to Ni₂P after TPR. According to gas analysis, the TPR process can be divided into three phases as depicted in Fig. 1. In Phase I and III, production of water was observed as two prominent desorption peaks, whereas water formation decreased monotonically in Phase II.

Figure 2 shows changes in the Fourier transform of EXAFS spectra ($k^3\chi(k)$) during TPR and Figure 3 depicts changes in coordination numbers (CN) estimated by curve fitting analysis of the corresponding EXAFS oscillations. In Phase I the Ni–Ni bonds substantially disappear and the Ni–O bonds decrease in number. In Phase II the decline in Ni–O bonds continues. In the early part of Phase III the free Ni atoms react with reduced P to form Ni₂P nuclei to form Ni–P bonds, rather than to become metallic Ni particles. Then crystal growth to form Ni₂P nanoparticles occurs, as confirmed by the emergence of the Ni–Ni bonds of Ni₂P.

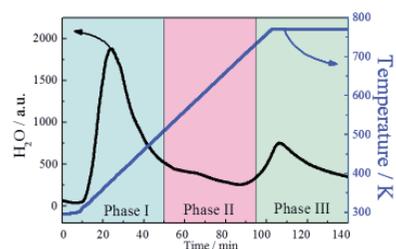


Figure 1
Desorption of water followed by an IR gas analyzer during TPR. Three phases are observed in the TPR process.

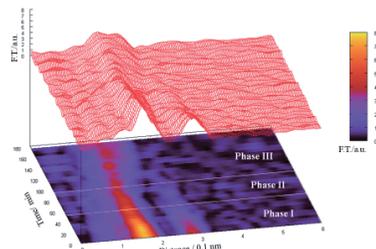


Figure 2
Change in Fourier transform of EXAFS spectra ($k^3\chi(k)$) during the TPR process.

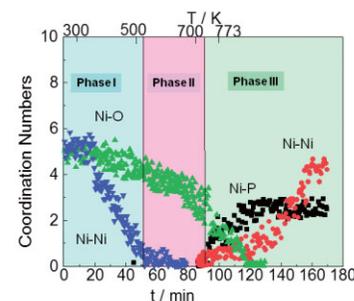


Figure 3
Change of coordination numbers during the TPR process. Green triangles are for Ni–O, and blue triangles are for Ni–Ni in Ni(OH)₂. Black squares are for Ni–P, and red circles are for Ni–Ni in Ni₂P.

Combining the results obtained by gas analysis and QXAFS, the structural change during TPR is considered to be as shown in Fig. 4. The decomposition of Ni(OH)₂ and stabilization of the atomically dispersed Ni species in Phase I and II enabled close contact of Ni with P species. In Phase III, the simultaneous reduction of Ni and P species occurred to form Ni₂P. The preferable forma-

tion of Ni–P over Ni–Ni prevented either the evolution of Ni metallic particles or further growth of Ni₂P particles. Stabilization of Ni²⁺ in Phase I and II is found to be requisite for the formation of Ni₂P.

It is important to understand such transient structural changes which determine the final state of the material, but the changes can be obtained only by a time resolved in situ technique. This work proved that combined analysis of gas phase products and QXAFS spectra is a powerful technique for clarifying detailed microscopic structural changes during a chemical process.

REFERENCE

- [1] K.K. Bando, Y. Koike, T. Kawai, G. Tateno, S.T. Oyama, Y. Inada, M. Nomura and K. Asakura, *J. Phys. Chem. C* **115** (2011) 7466.

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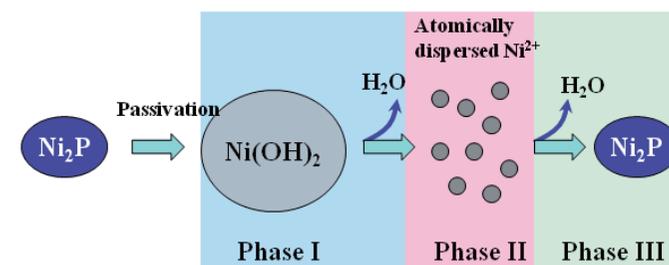


Figure 4
Proposed structural transformation during TPR.