学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

X-ray absorption spectroscopy studies on the structure and the catalytic activity of nickel phosphide catalysts

(X 線吸収分光法によるニッケルリン化物触媒の構造と触媒特性の研究)

X-ray absorption fine structure (XAFS) spectroscopy is the most promising technique for the atomic-level characterization of the inorganic-oxide-supported catalysts. It provides us element-specific detail information on the electronic state and the local structure. As XAFS can characterize local structure accurately even if the long-range order is not present in the sample, we can obtain the electronic and structural information on the powder or the solution samples by XAFS analysis. XAFS is composed of both X-ray Absorption Near Edge Structure (XANES) appearing near X-ray absorption edge and Extended X-ray Absorption Fine Structure (EXAFS) appearing above the edge from 50 eV to 1000eV. Although the EXAFS analysis has been established using the curve fitting (CF) method, the EXAFS analysis has a demerit in the structural analysis of complex structures caused by the Nyquist theory. I have applied the XAFS to determine the SiO_2-supported nickel phosphide (Ni-P) catalysts structures, which have been found to show the high activity for Non-Oxidative Coupling of Methane (NOCM) reaction. The NOCM is now an essential reaction because CH_4 is a good candidate for the alternative feedstock of petroleum to produce organic materials. Ni-P catalytic structures have a strong Ni:P ratio dependence on their activities. Ni_2P/SiO_2 (Initial Ni:P=1:1) shows the most effective conversion of CH_4 to higher hydrocarbons for NOCM, indicating the structure of Ni-P catalysts depends on the Ni:P ratio. However, nickel phosphide compounds have a complex structure, and it is challenging to decide the structure of the Ni-P catalyst exactly. In my doctoral work, I have revealed the structures of nickel phosphide catalysts and their composition dependence on catalytic activities using XAFS.

In Chapter 1, the synchrotron radiation-based X-ray absorption fine structure (XAFS) has been discussed briefly, followed by the discussion about the catalytically important silica-supported nickel phosphide catalyst for Non-Oxidative Conversion of Methane (NOCM) reactions.

In chapter 2, the experimental and general analysis methods using the CF method for EXAFS have been discussed. Then I discuss the theoretical model by FEFF method to analyze XAFS (EXAFS and XANES) of the Ni-P complex system.

In chapter 3, the active phase of Ni phosphide for NOCM has been determined by the conventional CF method using EXAFS data. The Ni-P catalyst with Ni:P=1:1 has the EXAFS oscillation and Fourier transform (FT) peak positions corresponding to the reference compound of Ni_2P. Thus the catalyst is characterized to be Ni_2P structure. But the other Ni-P structure with different Ni and P ratios of 2:1 and 3:1 cannot be determined by the CF method due to the complicated structure with various bond distances and lack of reference compounds. I discuss the limitation of the conventional method.

In chapter 4, the experimental XANES data analysis of Ni-P catalysts with different Ni and P ratios of

1:1, 2:1, and 3:1 has been analyzed. The experimental XANES data were compared with theoretical reference compounds. I successfully determine the unknown structure of Ni-P catalysts with different Ni and P ratios by the XANES simulation. I extend the energy range to the EXAFS region, and I compare the experimental data with theoretically derived EXAFS data. This approach to the EXAFS analysis based on the theoretical model is different from the conventional CF method, and I discuss the new approach of EXAFS analysis. Finally, I confirm the silica-supported Ni-P catalysts structures with various compositions and discuss the structure-activity relations.

In chapter 5, the brand new full potential multiple scattering (FPMS) method for XANES analysis to improve the conventional FEFF method has been discussed. I have applied FPMS in Ni phosphide complex system. The FPMS-calculated results of Ni_2P are compared with the conventional FEFF method. The FPMS is less convenient and complicated for XANES analysis than the FEFF method. I discuss future aspect of FPMS.

In chapter 6, I summarize the XAFS analysis of the Ni-P catalysts. I discuss the different analysis methods adopted here to determine the complicated structure and to derive the structure-activity relations. The prospects of my research are also discussed in this chapter.

In my Ph.D. research, I applied XAFS (XANES and EXAFS) technique in the complex nickel phosphide catalysts for NOCM reactions using a conventional EXAFS curve fitting method and a theoretical model method to make the relationship between the structure and the activity of Ni-P catalysts. This work shows the advantages of the theoretical model method to determine the complex heterogeneous catalysts, the exact structures of which were difficult to be determined by the conventional CF method. In addition I discuss a brad new analysis method of FPMS applied to catalytic system. I believe my work opens a new way to analyze the complex structure of heterogeneous catalysts more precisely.