

Local structure analysis of zeolite-supported Ni and Co sulfide catalysts possessing a high HDS activity by means of X-ray absorption spectroscopy

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Introduction

Recently, regulation of sulfur content in light oil has become severer to reduce particulate materials and SO_x in exhaust. For these purposes, development of new catalysts for ultra-deep-HDS treatment is strongly needed now. Currently, Co-Mo sulfide catalysts are used for HDS treatment. Recently, it was reported that Co sulfide catalysts supported on smectite, NaY and USY zeolite also show high HDS activities. Since these Co sulfide catalysts are supported on high-surface area supports, it is assumed that high dispersion of Co sulfides causes their high HDS activities. It is of great importance to study the catalytic properties of atomically dispersed Co sulfide species to disclose the origin of the catalytic synergies between Co and Mo sulfides and to provide rational bases for the design of highly active HDS catalysts. In this study, we report local structure of highly dispersed Co and Ni sulfide clusters supported in Na-type zeolites.

Experimental

Co/USY, Ni/NaY and Ni/USY catalysts were prepared by an impregnation method using Co(NO₃)₂ and Ni(NO₃)₂. The sample was sulfided at 673 K. The sulfided sample was evacuated at 673 K and transferred to an EXAFS cell with two Kapton windows without exposing to air. Co and Ni K-edge EXAFS spectra were measured at BL-10B in a transmission mode. The synchrotron radiation was monochromatized by a Si(311) monochromator.

Results and Discussion

Fig.1 shows Co K-edge XANES spectra for Co sulfide catalysts. The spectrum of CoS/USY-Na catalyst prepared by the impregnation method shows a sharp peak about 7725 eV. The peak intensity is stronger than that for CoS_x/USY-Na catalyst prepared by the CVD method. This result indicates that Co sulfides in the catalyst prepared by the impregnation method interact with the acid sites of the zeolite according to the following equation.

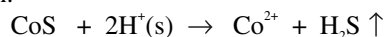


Fig.2 shows Ni K-edge XANES spectra for Ni sulfide catalysts. The spectrum of NiS/NaY catalyst prepared by an ion-exchange method shows very strong peak about 8355 eV. But the intensity of the peak for NiS/USY-Na and NiS/NaY catalysts prepared by the impregnation method are very weak. This is due to the variation in the amount of acid sites of zeolite and the reaction of Ni sulfide clusters with them.

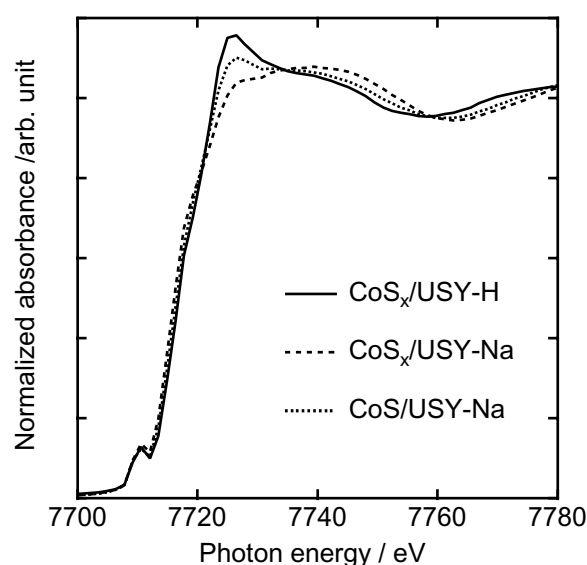


Fig.1 Co K-edge XANES spectra for Co sulfide catalysts prepared by an impregnation method and a CVD method.

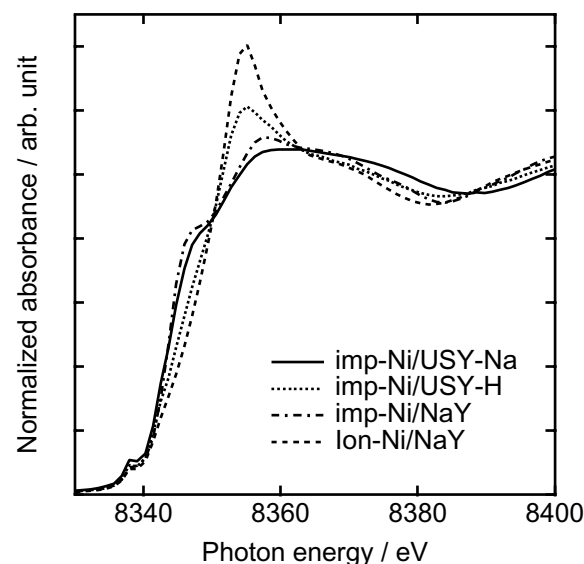


Fig.2 Ni K-edge XANES spectra for Ni sulfide catalysts prepared by an impregnation method and an ion-exchange method.

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