Structure of tungsten sulfide clusters encaged in NaX type zeolite and catalytic activity for the HDS of thiophene

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Tungsten sulfidfe clusters encaged in zeolites were successfully prepared by means of a CVD technique using $W(CO)_6$ as a precursor. It was found that the amount of tungsten was increased up to 1.7 atoms/SC. The catalyst color of WS_x/NaX (0.17 W/SC) turned to yellow after the sulfidation at 673 K for 1.5 h. The structure of W sulfide species in WS_x/NaX was studied by XAFS. It is proposed that the catalytic activity of the W sulfide clusters depends on the zeolite composition.

Introduction

In our previous studies, we succeeded in the preparation of molybdenum sulfide [1], oxide [2] and nitride [3] clusters encapsulated in NaY zeolite by means of a CVD technique using $Mo(CO)_6$ as a precursor. Highly dispersed molybdenum sulfide clusters with well-defined structures are easily synthesized at a low temperature when $Mo(CO)_6$ is used as a precursor. The Mo-Mo distance and catalytic activity was correlated for the molybdenum sulfide clusters encaged in zeolite with a various Si/Al ratio [4].

Productions of sulfur free petroleum fuels are becoming important in industry to protect environments. Hydrodesulfurization (HDS) has been carried out using sulfide catalysts consisting of Mo promoted with Ni or Co, or W promoted with Ni. Tungsten sulfide catalysts have been used for HDS reaction in recent years. SiO_2-supported Co–Mo and Co–W sulfide catalysts were characterized by NO adsorption, TEM, XPS, W L_3-edge XANES, and the measurements of the magnetic susceptibility and effective magnetic moment of Co [5].

Since the preparation of highly dispersed W-based sulfide catalysts is becoming increasingly important for deep HDS, we investigated the structure and HDS activity of tungsten sulfide clusters to obtain more detailed knowledge about their preparation chemistry.

Experimental

NaX zeolite was evacuated at 673 K for 1 h before a chemical vapor deposition (CVD) of $W(CO)_6$ at room temperature (RT) for 5 min - 3 h. The sample was sulfided in a stream of H_2 / H_2S = 90 / 10 ml•min^{-1} at 673 K for 1.5 h. The amount of tungsten anchored in zeolite was analyzed by XRF (Shimazu EDX-700HS). Pore volumes of WS_x/NaX were measured by benzene adsorption at 298 K on a BELSORP 18 PLUS (Nippon Bel). The W L_3-edge XAFS spectra of the catalysts were carried out at BL10B of KEK-PF in a transmission mode at RT using an in situ cell with Kapton windows. The synchrotron radiation was monochromatized by a Si(311) monochromator. The EXAFS data were analyzed using a program “Rigaku EXAFS 2000 (REX 2000)”.

The sulfided catalyst was evacuated at 673 K for 1 h before catalytic reaction. The catalytic activity was measured at 623 K for the HDS of thiophene. The HDS reaction was performed using a closed circulation system as reported previously [5]. The HDS activity was calculated on the basis of the amount of H_2S evolved.

Results and Discussion

When NaX zeolite was exposed to $W(CO)_6$ for 5 min, the W-loading was 0.17 atoms in supercage (SC). The sulfided sample is denoted WS_x-5m/NaX. The amount of W content in NaX was increased linearly up to 10 wt% after a 3 h exposure (W/SC: 1.7). The sample is denoted WS_x-3h/NaX. The pore volume of zeolite was decreased with increasing amount of W loading. It is proposed that the W sulfide clusters are encapsulated in NaX zeolite after the sulfidation. The catalyst color of WS_x-5m/NaX turned to yellow after the sulfidation. It is interesting to study the structure of W species in WS_x-5m/NaX. Figure 1 shows the W L_3-edge XANES spectra for WS_x/NaX. The fine structures around 10220 eV are different from those of a WS_2 reference. Figure 2 shows Fourier transforms (FT) of k^3-weighted EXAFS oscillations for WS_x/NaX. The FT peaks at 0.18, 0.20 and 0.25 nm in WS_x-3h/NaX are assigned to W-O, W-S and W-W, respectively. Comparing WS_x-3h/NaX and WS_x-5m/NaX, WS_x-5m/NaX shows no W-W peak around 0.25 nm. It is suggested that W sulfide or carbide monomeric species is formed in WS_x-5m/NaX.

Figure 3 shows a correlation between the amount of W loading and TOF (HDS activity / W atom) for WS_x/NaX and WS_x/USY-Na. The TOF of WS_x/USY-Na was decreased with increasing of W loadings. It seems that the HDS of thiophene on WS_x/USY-Na is diffusion controlled. On the other hand, the TOF of WS_x/NaX was increased with increasing W loadings up to 1 W atom/SC, followed by a gradual decrease. It is proposed that the structure of tungsten sulfide species strongly affect the TOF.

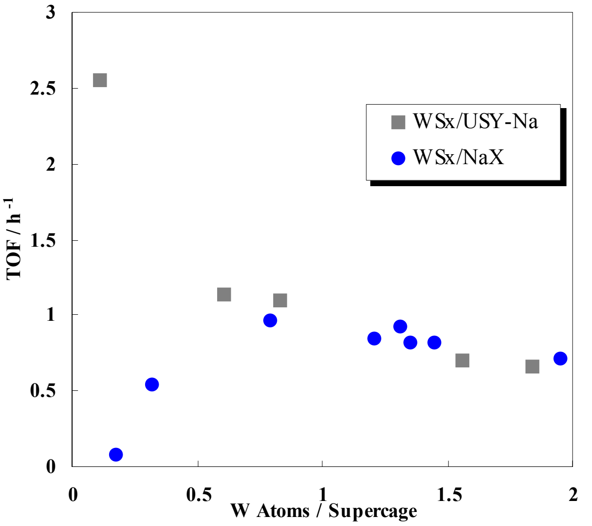

Figure 3 TOF of HDS activity on WS_x/NaX and WS_x/USY-Na as a function of W loading

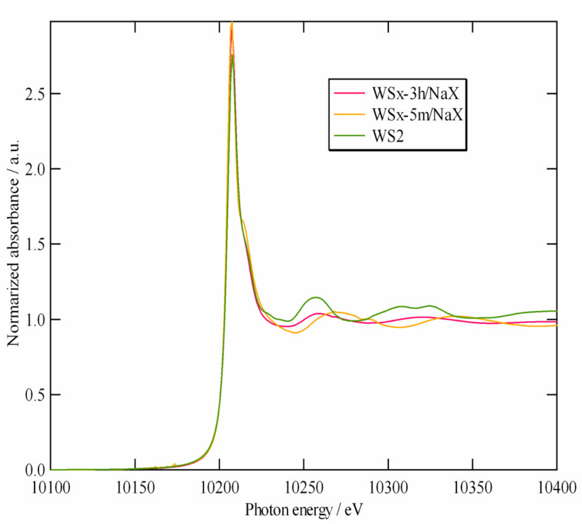

Figure 1 W L_3-edge XANES spectra for WS_x/NaX as a reference

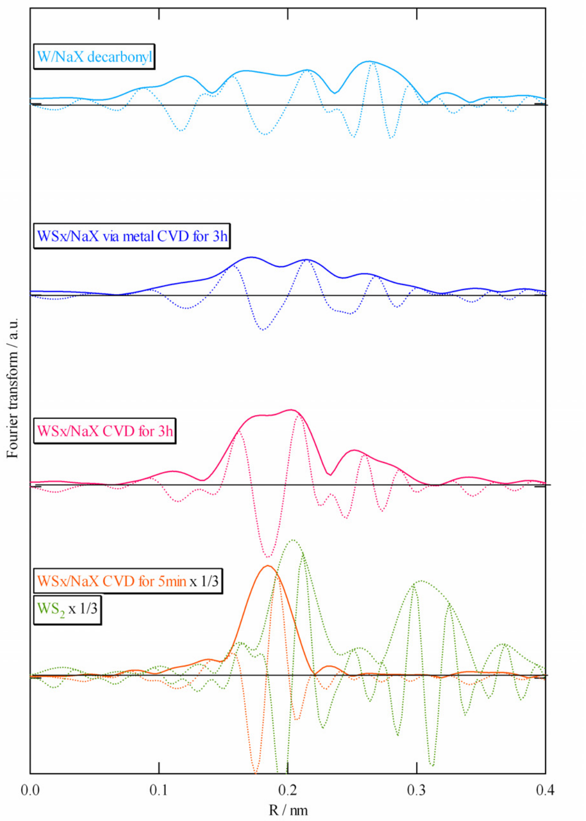

Figure 2 Fourier transforms of k^3-weighted EXAFS oscillations for WS_x/NaX

References

[1] Y. Okamoto and T. Kubota, Catal. Surv. Jpn., 5 (2001) 3.

[2] Y. Okamoto, N. Oshima, Y. Kobayashi, O. Terasaki, T. Kodaira, T. Kubota, Phys. Chem. Chem. Phys., 4 (2002) 2852.

[3] T. Kadono, T. Kubota, Y. Okamoto, Catal. Today, 87 (2003) 10.

[4] T. Kadono, T. Kubota, H. Chatani, T. Kawabata, and Y. Okamoto, Stud. Surf. Sci. Catal., in press.

[5] Y. Okamoto, A. Kato, Usman, K. Sato, I. Hiromitsu, T. Kubota, J. Catal., 233 (2005) 16