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In situ XAFS analysis of catalytically active cobalt species in porous clays for deep hydrodesulfurization

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Abstract

Mesoporous smectite-type clays containing cobalt species in lattice (MST(Co)) were prepared by a hydrothermal method and examined for hydrodesulfurization (HDS). The MST(Co) catalysts showed higher HDS activities than a commercial alumina-supported cobalt–molybdenum catalyst (Co–Mo/Al_2O_3). The active structure of MST(Co) was studied by in situ X-ray absorption fine structure and nitrogen adsorption techniques.

Keywords: XAFS analysis; Hydrodesulfurization; Cobalt species

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1. Introduction

Hydrodesulfurization (HDS) treatment is an important process for producing clean fuel. Supported Co–Mo catalysts have been used for HDS of petroleum feedstock [1]. There are also several reports, which claimed that Co alone could be highly active for HDS. Vissers et al. [2] reported that highly dispersed Co sulfide species supported on carbon exhibited a high hydrodesulfurization activity as high as Co–Mo binary sulfide catalysts. de Bont et al. [3] reported that a NaY supported cobalt catalyst prepared by an ion-exchange method showed a high initial HDS activity. Kubota et al. [4] reported that zeolite supported highly dispersed cobalt sulfide clusters showed a much higher HDS activity than conventional alumina-supported Co–Mo catalysts. It is of great importance to design Co catalysts highly active for HDS and to elucidate the mechanism how these active Co species work during the reaction.

Smectite is one of the layered clay minerals. A relatively simple hydrothermal method is applicable to the synthesis of mesoporous smectite-type clays (MST) containing several divalent cations in lattice [5]. We have also showed that mesoporous smectite-type clays containing cobalt cations in lattice (MST(Co)), were highly active for thiophene hydrodesulfurization [6,7]. In this paper, we report preparation, hydrodesulfurization activities, and in situ X-ray absorption fine structure (XAFS) analysis of MST(Co) catalysts.

2. Experimental

MST(Co) catalysts were prepared by procedures similar to those used previously [6,7]. Water glass ($SiO_2/Na_2O = 3.22$) solution was mixed with

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sodium hydroxide solution. Cobalt chloride solution was added to this solution while stirring the mixture, producing a Co–Si precipitate, in which the Si:Co atomic ratio was adjusted to 8:5.8 by using the desired volumes and concentrations of the starting solutions. After filtration and washing with water, water was added again to the precipitate. Then the slurry was thermally treated in an autoclave under autogaseous pressure. After drying and calcination, mesoporous clays (MST(Co)) were obtained.

HDS activities of catalysts were evaluated by two methods. The initial HDS activity of thiophene was measured using a closed circulation system at 623 K. The sample was treated in a 10% H_2S/H_2 flow (100 ml min^{-1}) at 673 K for 1.5 h before HDS. Thiophene was introduced into the reactor at the saturation vapor pressure of 273 K, and then H_2 was supplied to the system until the ratio of thiophene/H_2 became 1/10 (total pressure: 22 kPa). The thiophene/hydrogen ratio was kept almost constant during the reaction. The reaction products were analyzed by an on-line gas chromatograph with a thermal conductive detector (TCD). The initial HDS activity was evaluated from the initial rates for H_2S production.

A quartz fixed-bed flow reactor was used to evaluate the steady-state HDS activity of the catalysts. After treatment with a 10% H_2S/H_2 flow (100 ml min^{-1}) at 673 K for 1.5 h, the HDS reaction was started by introducing 2.9% thiophene/H_2 (22 ml min^{-1}). The reaction products were analyzed by an on-line gas chromatograph with a flame ionization detector (FID). Although H_2S was a main product of HDS, the FID detector is not applicable to analysis of inorganic gases like H_2S. Therefore, the HDS activity was estimated from the amount of hydrocarbons. The activity after 6 h of the reaction was regarded as the steady-state HDS activity.

The surface areas of samples were measured by nitrogen adsorption. The bulk chemical composition was determined by X-ray fluorescence analysis. Co K-edge XAFS measurements were made in a transmission mode at BL-7C of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan. The catalyst was pressed into a round disc and was set in an in situ cell designed for measurements under a reactant gas [8]. In situ XAFS spectra were obtained during pre-treatment under a 5% H_2S/H_2 flow (60 ml min^{-1}) from 423 to 673 K and a subsequent reaction under 1.8% thiophene/H_2 flow (60 ml min^{-1}) at 623 K. The transmission spectra were collected using ionization chambers that were filled with nitrogen gas. Extended X-ray absorption fine structure (EXAFS) oscillation was extracted from the raw data by background subtraction using a cubic spline method and normalization with the edge height. The k^3-weighted EXAFS spectra were Fourier transformed to R space, where "k" indicates a photoelectron wave number and "R" represents a distance between the absorber atom and a scatterer atom.

3. Results and discussion

Fig. 1 shows the ex situ XRD patterns of an MST(Co)523 sample (a clay sample hydrothermally synthesized at 523 K) drying at 353 K (a) and calcined at 873 K (b). The positions of the peaks appearing in XRD patterns of the both MST(Co) samples were identical to natural smectite-type materials [9] and the peaks ascribed to cobalt oxide (Co_3O_4) were not observed in the diffraction patterns of MST(Co) samples. Therefore, the XRD analysis indicated that all the cobalt species were incorporated into the lattice and the MST(Co) samples were composed solely of silicate fragments having smectite structure. All peaks in the XRD patterns of MST(Co) samples, especially the (0 0 1) peaks, were very weak compared with those of natural smectite-type clays, indicating that silicate fragments in MST samples were small and not

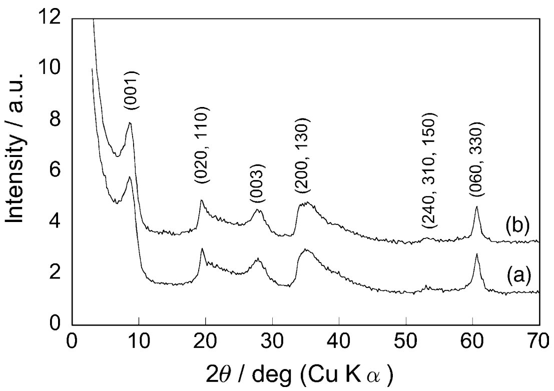

Fig. 1. The XRD patterns of MST(Co)523. (a) Drying at 353 K and (b) calcined at 873 K.

Table 1
Surface area and chemical composition of MST(Co) samples

Sample code	Hydrothermal temperature (K)	Hydrothermal time (h)	Surface area[a] ($m^2 g^{-1}$)	Composition Si:Co:Na
MST(Co)473	473	4	451 (287)	8:5.1:0.09
MST(Co)523	523	4	214 (126)	8:5.4:0.11

[a] BET surface area measured by nitrogen adsorption before and after (values in parentheses) HDS reaction.

Table 2
Comparison of initial HDS activities at 623 K of MST(Co) and commercial Co–Mo/Al_2O_3 catalysts

Sample code	Initial HDS activity ($\times 10^{-5}$ mol g^{-} cat^{-1} h^{-1})
MST(Co)473	642
MST(Co)523	478
G-51B	246

stacked in parallel so well as in natural smectite-type clays. The surface area of natural smectite-type clays is less than 20 $m^2 g^{-1}$ [10] however, that of the MST(Co) was much larger (Table 1). Generally speaking, pillared clays are thermally stable and keep their large surface area around 200–500 $m^2 g^{-1}$ even above 773 K, because small oxide particles (pillars) induce micropores in montmorillonite [11]. In the case of MST(Co), smectite-type crystal is the only phase. Therefore it is suggested that silicate fragments having smectite structure were intercalated between silicate layers and formed mesopores in the clay, which resulted in the high thermal stability and the large surface area. The surface area of the synthetic clay synthesized at 473 K, MST(Co)473, was larger than that of MST(Co)523, suggesting that the size of silicate fragments in the MST(Co)473 sample is smaller than that in MST(Co)523 [5]. Also, large surface area values of MST(Co) samples were maintained after HDS reaction.

MST(Co) samples showed higher activities for the both initial and steady-state HDS reactions than a conventional silica-supported catalyst (Co/SiO_2) and a commercial catalyst (Co–Mo/Al_2O_3) (Tables 2 and 3). The product distribution of synthetic MST(Co) samples was similar to that of the Co/SiO_2, suggesting that the nature of HDS active sites in the former is not the same as that of the latter. The high activity of MST(Co) samples should be owing to a high degree of cobalt dispersion. During preparation, Co atoms were introduced as cations into a lattice of silicate fragments having smectite-type structure for MST(Co) samples. The exposed cobalt species at the edge of the silicate fragments were sulfided and formed active sites for HDS. The MST(Co)473 catalyst having larger surface area showed higher HDS activities than that of MST(Co)523, because synthetic clays with larger surface area are composed of many smaller silicate fragments and have much exposed edge sites of the silicate fragments.

Fig. 2 shows the in situ XANES spectra for MST(Co)523 samples before (a) and during sulfidation from 423 to 673 K ((b)–(d)) and HDS reaction at 623 K (e). XANES spectrum of cobalt sulfide (Co_9S_8) (f) is also shown. Although the intensity of the white line around 7720 eV slightly decreased with

Table 3
Comparison of steady-state activities for HDS at 623 K

Sample code	Steady-state conversion (%)	Selectivity (%)			
		n-Butane	1-Butene	*Trans*-2-butene	*Cis*-2-butene
MST(Co)473	41	8	18	42	30
MST(Co)523	37	7	18	42	31
35% Co/SiO_2[a]	23	5	23	41	30
G-51B[b]	28	18	17	35	26

[a] The amount of cobalt on silica (35 wt.%) is the same as that of MST(Co) samples.

[b] Commercial catalyst: CoO 3.5 wt.%, MoO_3 10 wt.%.

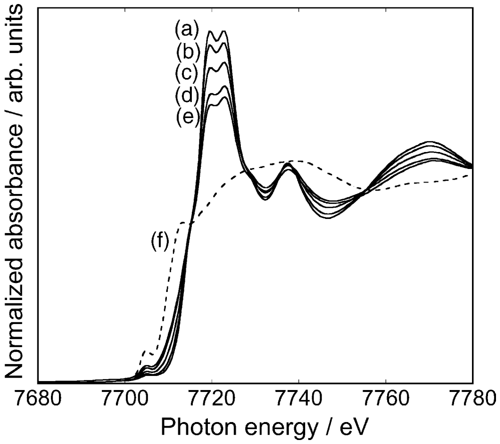

Fig. 2. In situ Co K-edge XANES spectra of the MST(Co)523 samples: (a) fresh, (b) sulfided at 423 K, (c) 573 K, (d) 673 K, (e) during HDS at 623 K, (f) Co_9S_8 (dashed line).

increasing sulfidation temperature, the shape of the white line was similar to that of the fresh MST(Co)523 catalyst during sulfidation and totally different from that of cobalt sulfide. Fig. 3 shows the Fourier transforms of in situ EXAFS spectra for MST(Co)523 samples before (a) and during sulfidation from 423 to 673 K ((b)–(d)) and HDS reaction at 623 K (e). Two peaks were observed in all the Fourier transforms of EXAFS spectra of the MST(Co) samples (phase shift uncorrected); the peaks between 0.1 and 0.2 nm are ascribed to Co–O bond and the peak between 0.2 and 0.3 nm are ascribed to the Co–O–Co and Co–O–Si bonds. The intensities of two peaks decreased with increasing treatment temperature. The decrease of the intensity of Co–O and Co–O–Co bonds would be explained by the effect of temperature. The EXAFS spectra of the samples sulfided (Fig. 3(b)–(d)) were measured at the each treatment temperature. Peak intensities of the EXAFS Fourier transforms at higher measurement temperature became lower by Debye–Waller factor. The EXAFS spectra of MST(Co) during HDS and cobalt sulfide were measured at 623 K (Fig. 3(e) and (f)). No peak derived from sulfides was observed in the EXAFS Fourier transforms of the MST(Co) samples, indicating that cobalt sulfide particles were not formed. The Co–S bonds were not observed because the number of cobalt atoms located at the edge sites is small. Nitric oxide adsorption analysis showed that 10% of cobalt was exposed for a fresh MST(Co)523 catalyst, indicating that only 10% of cobalt was located at the edge of silicate fragments. XANES and EXAFS analysis also show that the 10% of cobalt in the MST(Co)523 sample do not form small sulfide particles, because the XANES and EXAFS spectra of cobalt sulfide are totally different form those of MST(Co) samples. Because of the partially sulfided structure and low concentration, information about the structure of surface cobalt species of silicate fragments in the MST(Co) catalysts could not be obtained from the in situ XAFS analysis.

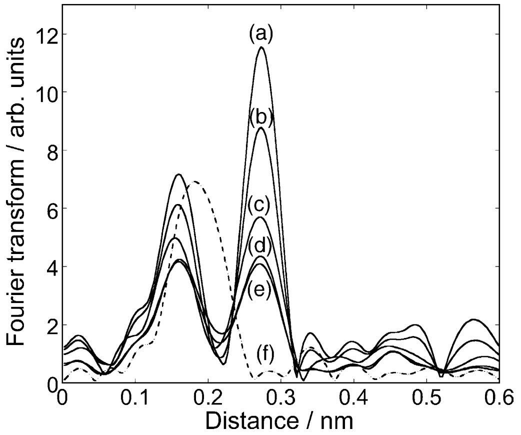

Fig. 3. Fourier transforms of in situ Co K-edge EXAFS oscillations for MST(Co)523: (a) fresh, (b) sulfided at 423 K, (c) 573 K, (d) 673 K, (e) during HDS at 623 K, (f) Co_9S_8 (dashed line).

Nitrogen adsorption and in situ XAFS analysis indicated that the bulk structure of silicate fragments of synthetic clays was stable and only the edge sites would be sulfided. By changing hydrothermal conditions, we could design MST(Co) samples consisting of many smaller silicate fragments and they would show high HDS activity because of exposing many active edge sites.

4. Conclusions

Mesoporous smectite-type clays containing cobalt species in lattice (MST(Co)) prepared by a hydrothermal method showed higher thiophene hydrodesulfurization activities than a commercial alumina-supported cobalt–molybdenum catalyst. In situ XAFS and nitrogen adsorption techniques showed that surface cobalt species located at the edge of silicate fragments of MST(Co) were the active sites.

Acknowledgements

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