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Characterization of highly dispersed cobalt sulfide catalysts by X-ray absorption fine structure and magnetic properties

Takeshi Kadono, Takeshi Kubota, Ichiro Hiromitsu, Yasuaki Okamoto *

Department of Material Science, Shimane University, Matsue 690-8504, Japan

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Abstract

Zeolite-supported cobalt sulfide catalysts, CoS/NaY and CoS/USY-H, were prepared using $Co(CO)_3NO$ as a precursor. A SiO_2-supported cobalt sulfide catalyst was prepared by an impregnation method for comparison. The prepared catalysts were characterized by magnetic properties and XAFS. The cobalt sulfides in CoS/NaY are paramagnetic and can be characterized as intrazeolite dinuclear species with antiferromagnetic interactions between the Co atoms, in contrast to the cobalt sulfides in CoS/SiO_2, in which 95% of Co is Co_9S_8 and 5% is paramagnetic with a very small amount of ferromagnetic species. The structure of the cobalt sulfides in CoS/USY-H depends on the treatment after the sulfidation. Ultra-highly dispersed cobalt sulfide species initially formed during the sulfidation are transformed to highly dispersed Co_9S_8-like particles and eventually to ion-exchanged Co^{2+} cations as the evacuation temperature and duration are increased. The catalytic activity of the cobalt sulfide catalysts was measured for the hydrodesulfurization of thiophene. The results suggest a synergy generation between cobalt sulfides and surface hydroxyl groups.

Keywords: Cobalt sulfide catalysts; Hydrodesulfurization; Magnetic property; XAFS; XANES; Zeolite

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1. Introduction

Cobalt-promoted molybdenum sulfide catalysts have been used in industry for hydrotreating petroleum feedstocks [1–3]. Numerous studies have been conducted to disclose the nature of the synergy generation between cobalt and molybdenum sulfides [2–7]. Topsøe and coworkers [2,7–10] have proposed the so-called Co–Mo–S structure as the active sites, in which Co atoms are highly dispersed and located on the edge of MoS_2 particles. Recently, on the basis of their Mössbauer study, Crajé et al. [11–14] suggested the formation of cobalt sulfide clusters in contact with MoS_2 particles as the origin of the catalytic synergy in Co–Mo sulfide catalysts supported on activated carbon and alumina. However, the roles of the cobalt sulfides in these active site models in hydrodesulfurization (HDS) reactions have not been clarified yet. The physicochemical and catalytic properties of highly dispersed cobalt sulfide catalysts have received considerable attention up to now [15–20].

One of the promising preparation methods of highly dispersed cobalt sulfide species is to use zeolite as a support because of its high surface area and homogeneous pore structure [21–24]. de Bont [25–27] and Welters et al. [28] showed that when a Co^{2+} ion-exchanged NaY (Co^{2+}-NaY) zeolite was carefully sulfided in the absence of H_2O, finely dispersed Co sulfide clusters are formed in the zeolite cages; charge compensating hydroxyl groups are simultaneously formed. However, the Co sulfide clusters were instable at a high temperature in the absence of H_2S because of the reaction between the Co sulfide clusters and the hydroxyl groups to form H_2S and Co^{2+} cations in the zeolite (a reverse reaction of the sulfidation) [29,30]. In our previous study [31–34], highly dispersed Co sulfide clusters were prepared in NaY by using $Co(CO)_3NO$ as a precursor (CoS/NaY). EXAFS analysis suggested the formation of finely dispersed Co sulfide species, possibly Co dinuclear sulfide clusters [33]. In the present study, the magnetic properties and XAFS of zeolite-supported cobalt sulfide clusters were measured and compared with those of a CoS/SiO_2 impregnation catalyst. We employed NaY and USY zeolites because of their wide use in industry and academia. The instability of cobalt sulfide clusters in H^+-type zeolite was also examined by XAFS.

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* Corresponding author. Tel.: +81 852 32 6466; fax: +81 852 32 6466.
E-mail address: yokamoto@riko.shimane-u.ac.jp (Y. Okamoto).

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2. Experimental

2.1. Catalyst preparation

Cobalt sulfide catalysts supported on NaY (CoS/NaY) were prepared by a chemical vapor deposition (CVD) technique using $Co(CO)_3NO$ as a precursor. NaY zeolite (Si/Al = 2.8) was supplied by the Catalysis Society of Japan as a Reference Catalyst (JRC-ZRO-5.6). The preparation method has been described elsewhere [32–34]. Briefly, a zeolite sample was evacuated at 673 K for 1 h and then exposed to a vapor of $Co(CO)_3NO$ (kept at 273 K) at room temperature for 5 min, followed by evacuation for 10 min at room temperature to remove physisorbed $Co(CO)_3NO$ molecules on the external surface of the zeolite particles. The sample was sulfided at 673 K for 1.5 h in a 10% H_2S/H_2 stream to prepare CoS/NaY. USY zeolite (ultra-stable Y-zeolite, Shokubai Kasei Kogyo Ltd., Si/Al = 3.6, H^+-type) was also used to prepare CoS/USY-H in a similar manner. The amounts of Co loading in CoS/NaY and CoS/USY-H were 5.8 and 3.9 wt.% Co, respectively, as measured by XRF (Shimadzu, EDX-700HS). A SiO_2-supported Co catalyst (3.9 wt.% Co) was prepared by a conventional impregnation technique using $Co(CH_3COO)_2$ as a starting material [35]. The SiO_2 support was supplied by the Catalysis Society of Japan as a Reference Catalyst (JRC-SIO-4, 347 m^2/g).

The initial catalytic activity of the freshly sulfided catalyst was measured for the HDS of thiophene at 623 K after evacuation at 673 K for 1 h. The HDS reaction was performed using a closed circulation system, as reported previously [34]. The reaction rate was evaluated from the amount of H_2S that accumulated in the reaction system. The initial pressure of H_2 was 26.6 kPa, while the vapor pressure of thiophene (2.6 kPa) was kept constant during the reaction.

2.2. Characterization

The Co K-edge XAFS spectra for the cobalt sulfide catalysts were measured at room temperature in a fluorescence mode at BL-9C of the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization. Each sample was evacuated at 673 K for 1 h, unless otherwise noted, after the sulfidation and transferred to an in situ EXAFS cell. The evacuation temperature and duration of CoS/USY-H were varied and are shown in parentheses, such as CoS/USY-H (673 K, 1 h). The XANES spectra of CoO/SiO_2, the precursor of CoS/SiO_2, were measured in air. The EXAFS parameters were calculated using FEFF code (8.2) for Co–Co, Co–S, and Co–O atomic pairs.

The static magnetic measurements of the sulfided catalyst were conducted in situ with a Faraday method using a Cahn 2000 Electro-Balance system between 77 and 300 K [36]. The catalyst sample was evacuated at 673 K for 1 h before being fused into a glass ampoule. The magnetic moment was obtained by subtracting the magnetic contributions of the glass ampoule and SiO_2 or NaY zeolite separately measured under the identical measurement conditions.

The pore volumes of the NaY zeolite and CoS/NaY were calculated from benzene adsorption at 298 K (Bel Japan Inc., BELSORP 18PLUS) using a Dubinin-Radushkevitch equation. The sample was evacuated at 673 K for 4 h ($<1 \times 10^{-3}$ Pa) before the adsorption. The detailed procedures have been reported elsewhere [37].

3. Results and discussion

3.1. Structure and HDS activity of cobalt sulfides in CoS/SiO_2 and CoS/NaY

Fig. 1 compares the catalytic activity of the cobalt sulfide catalysts for the HDS of thiophene at 623 K. CoS/NaY showed a 30% higher activity than CoS/SiO_2 in fair agreement with our previous study [34]. CoS/SiO_2 prepared from cobalt acetate showed a several times higher HDS activity than cobalt sulfide catalysts prepared from cobalt nitrate as a precursor [35]. CoS/SiO_2 showed almost the same intrinsic activity (activity per mole Co) with CoS/NaY. The pore volume of CoS/NaY was 0.26 cm^3/g and was smaller by 0.04 cm^3/g than the volume of NaY (0.30 cm^3/g), suggesting that a great majority of cobalt sulfides in CoS/NaY are located in zeolite pores.

The magnetic property of Co in CoS/NaY was measured to characterize the nature of the cobalt sulfide species in the catalyst. Fig. 2 presents the magnetic moment of Co in CoS/NaY at 77 and 300 K as a function of the external magnetic field. It is obvious that the magnetic moment of Co in Fig. 2 cannot be correlated to any theoretical equation by assuming a single kind of magnetic component, suggesting the presence of at least two kinds of magnetic components with different magnetic properties. When we assume the presence of paramagnetic and superparamagnetic cobalt sulfide species

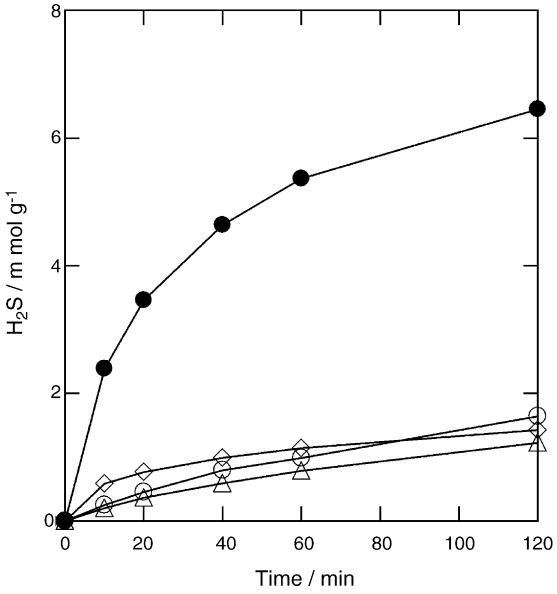

Fig. 1. The catalytic activity of CoS/NaY (○), CoS/SiO_2 (△), CoS/USY-H (●), and USY-H (◇) for the HDS of thiophene as expressed by the formation of H_2S as a function of reaction time.