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Hydrodesulfurization activity of highly dispersed Co sulfide clusters prepared in zeolite cages

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Zeolite-supported highly dispersed Co sulfide clusters are synthesized using $Co(CO)_3(NO)$ as a precursor. The amount of Co in CoS_x/zeolite anchored by a CVD technique increases as the Al/Si ratio of the zeolite increases, whereas the activity per Co atom decreases for thiophene hydrodesulfurization (HDS). When an Na-exchanged USY zeolite is used, the Co sulfide catalyst shows a much higher HDS activity than a conventional Co–Mo/Al_2O_3 catalyst. It is considered from XAFS and NO adsorption techniques that the high HDS activity of CoS_x/USY-Na is due to an extremely high dispersion of Co sulfide clusters.

Keywords: highly dispersed Co sulfide clusters, thiophene hydrodesulfurization (HDS), CVD method, XAFS, zeolite

1. Introduction

Hydrodesulfurization (HDS) treatment is an indispensable process to produce clean fuel, and Al_2O_3-supported Co–Mo sulfide catalysts have been extensively used for HDS of petroleum feedstocks [1,2]. It is well known that catalytic synergy generates between Co and Mo sulfides in the catalyst system. Numerous studies have been made to clarify the cause of the synergy effects by means of a variety of physicochemical techniques: EXAFS, Mössbauer emission spectroscopy (MES), XPS and so on [3–5]. On the basis of the MES study of Co–Mo/Al_2O_3 catalysts, Topsøe et al. [3,6] proposed that a “Co–Mo–S” phase is responsible for HDS activity. Bouwens et al. [7,8] studied the structure of the Co–Mo–S phase using Mo and Co K-edge EXAFS spectroscopy and concluded that the Co atoms in the Co–Mo–S phase are atomically dispersed and located, most likely in front of the square sulfur faces of the MoS_6 trigonal prisms along the edges of the MoS_2 crystallites. On the other hand, Vissers et al. [9] found that in spite of a single metal catalyst, highly dispersed Co sulfide species supported on activated carbon exhibit such a high HDS activity as Co–Mo binary sulfide catalysts. According to de Bont et al. [10], Co/NaY prepared by an ion exchange method shows a high initial HDS activity. Recently, it was reported that Co sulfide catalysts supported on smectite also show high HDS activities [11–14]. Since these Co sulfide catalysts are supported on high surface area supports, it is assumed that high dispersions of Co sulfides cause their high HDS activities. In Co/NaY [10] and smectite [14] systems, however, it is necessary to take into account the synergy effects between acidity of the support and Co sulfides. 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.

We have previously reported that Co sulfide clusters are prepared by sulfiding $Co(CO)_3(NO)$ encaged in an NaY zeolite [15,16]. It is shown by means of EXAFS analysis that these clusters are highly dispersed and highly active for thiophene HDS. Accordingly, by use of Na-exchanged zeolites as supports it is possible to examine intrinsic catalytic properties of highly dispersed Co sulfide clusters by excluding synergy effects caused by support acidity. In this paper, we report an extremely high HDS activity of high dispersed Co sulfide clusters synthesized in Na-type USY zeolites.

2. Experimental

Zeolite-supported Co sulfide catalysts were prepared by a CVD method using $Co(CO)_3(NO)$ as a precursor [15,16]. The zeolites (ca. 0.1 g) were evacuated at 673 K for 1.5 h and then exposed to a $Co(CO)_3(NO)$ vapor at room temperature for 5 min, followed by evacuation for 10 min at room temperature to remove physisorbed $Co(CO)_3(NO)$ on the external surface of the zeolite. The sample was then sulfided in a 10% H_2S/H_2 flow (100 $cm^3\,min^{-1}$) at 673 K for 1.5 h. The Co sulfide catalysts thus prepared are denoted CoS_x/zeolite. Zeolites used here are of Na-exchanged faujasite-type (NaX, NaY, USY-Na, dealuminated NaY (HSi-FAU) [17]). H-type USY zeolites (Syokubai Kasei) were repeatedly ion exchanged to produce Na-exchanged USY (USY-Na) using CH_3COONa until USY-Na showed such a low thiophene HDS activity as NaY. The compositions of representative zeolites used here are summarized in table 1. The sulfided catalyst was evacuated at 673 K for 1 h before thiophene HDS reaction and

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Table 1
Composition, thiophene HDS activity and NO adsorption capacity of CoS_x/zeolite.

Catalyst	Al/Si ratio	Co loading (wt%)	HDS activity[a]	NO/Co
CoS_x/USY-Na	0.23	5.9	243	0.92
CoS_x/NaY	0.36	6.3	98.2	0.75
CoS_x/NaX	0.81	7.7	55.3	n.m.[b]
CoS_x/FAU	0.002	1.5	60.9	n.m.
CoS/SiO_2[c]	0	3.9	50.6	0.51
CoS/Al_2O_3[c]	–	3.9	30.6	0.33
$CoS–MoS_2/Al_2O_3$[c,d]	–	1.6	179	0.20[e]

[a] Activity in 10^{-5} mol g-support^{-1} h^{-1}.
[b] Not measured.
[c] Prepared by an impregnation method.
[d] Mo 8.7 wt%.
[e] NO/(Co + Mo).

EXAFS measurements. Conventional CoS/Al_2O_3, $CoS–MoS_2/Al_2O_3$ and CoS/SiO_2 sulfide catalysts were prepared by impregnating Al_2O_3 (JRC-ALO4 [18], 177 m^2 g^{-1}) or SiO_2 (JRC-SIO-4 [18], 347 m^2 g^{-1}) with aqueous solution of $Co(CH_3COO)_2$ and $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ and calcined at 773 K for 5 h, followed by sulfidation at 673 K for 1.5 h.

The HDS reaction of thiophene was performed using a closed circulation system at 623 K [15,16]. In the case of the HDS reaction, a vapor pressure of thiophene at 273 K was used and the thiophene/H_2 ratio (1/10, total pressure 30 kPa) was kept almost constant during the reaction. The reactants and products were analyzed by gas chromatography. The catalytic activity was obtained from the initial rate for H_2S production (mol g-support^{-1} h^{-1}).

The Co loadings of the CoS_x/zeolite samples were determined by XRF (Rigaku, RIX2000). Nitric oxide adsorption measurements for freshly sulfided catalysts were carried out at room temperature using a pulse technique. The Co K-edge EXAFS spectra for the CoS_x/zeolite samples were measured in a transmission mode at BL-10B of Photon Factory in Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The sulfided sample was evacuated at 673 K and transferred to an EXAFS cell with two Kapton windows without exposing to air.

3. Results and discussion

Table 1 shows the initial HDS activities of CoS_x/zeolite, CoS/Al_2O_3 and $CoS–MoS_2/Al_2O_3$ catalysts. Obviously, CoS_x/USY-Na shows the highest activity for the thiophene HDS reaction. The activity of USY-Na was very low and close to that for NaY or NaX, excluding a direct contribution of the support to the HDS activity of CoS_x/USY-Na. It is worthy to note that the performance of CoS_x/USY-Na exceeds that of $CoS–MoS_2/Al_2O_3$ in spite of a single component system.

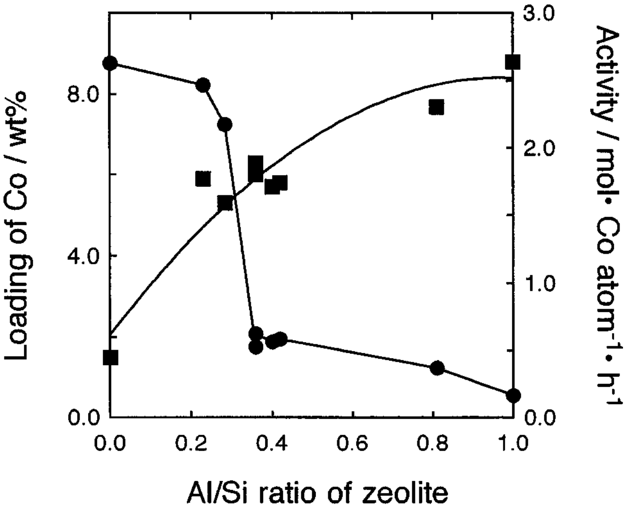

Figure 1. The activity per Co atom of the HDS reaction (●) and loading of Co (■) for CoS_x/zeolite as a function of the Al/Si ratio of the host zeolite.

To clarify the origin of the extremely high activity of CoS_x/USY-Na, the effect of the zeolite composition of CoS_x/zeolite was examined on the HDS activity. The activity per Co atom of the HDS reaction (mol Co-atom^{-1} h^{-1}) is plotted in figure 1 against the Al/Si ratio of the zeolite. The amount of Co in CoS_x/zeolite anchored by the present CVD technique is also shown in figure 1. It is revealed that the loading of Co increases as the Al/Si ratio of the host zeolite increases. This may be a consequence of stronger interactions between $Co(CO)_3(NO)$ molecules and the zeolite framework with a higher Al/Si ratio. On the other hand, it is evident that the HDS activity per Co atom increases as the Al/Si ratio of the support decreases. Especially, the Co sulfide catalysts supported on USY-Na and dealuminated zeolite (HSi-FAU) show very high activity per Co atoms, compared with CoS_x/NaY or CoS_x/NaX. It is considered that the Al/Si ratio or the acidity/basicity of the host zeolite [19] determines the Co loading and catalytic property of the resultant Co sulfide clusters.

Figure 2 compares the Fourier transforms of k^3-weighted Co K-edge EXAFS oscillations for CoS_x/NaY, CoS_x/USY-Na and Co_9S_8. In the Fourier transforms a common peak appears between 1 and 2 Å, which is assigned to Co–S bondings. A second peak at about 2.2 Å (phase shift, uncorrected) is assigned to Co–Co bondings. With CoS_x/zeolite, absence of FT peaks between 3 and 4 Å characteristic of Co_9S_8 indicates that highly dispersed Co sulfide clusters are constructed in accordance with the results of NO adsorption measurements in table 1. Since the intensity of FT peaks at about 2.2 Å for CoS_x/USY-Na is about a half of that for CoS_x/NaY, it is inferred that CoS_x/USY-Na has a lower Co–Co coordination number than CoS_x/NaY, where Co sulfide species are present as dimer clusters [15]. Therefore, it is presumed that dispersion of Co sulfide species is strongly affected by the Al/Si ratio of the host zeolite and that most of the Co sulfide species in CoS_x/USY-Na is atomically dispersed. These results lead us to conclude that the extremely high activity of CoS_x/USY-Na can be attributed to the formation of atomically dispersed Co sulfide clusters.

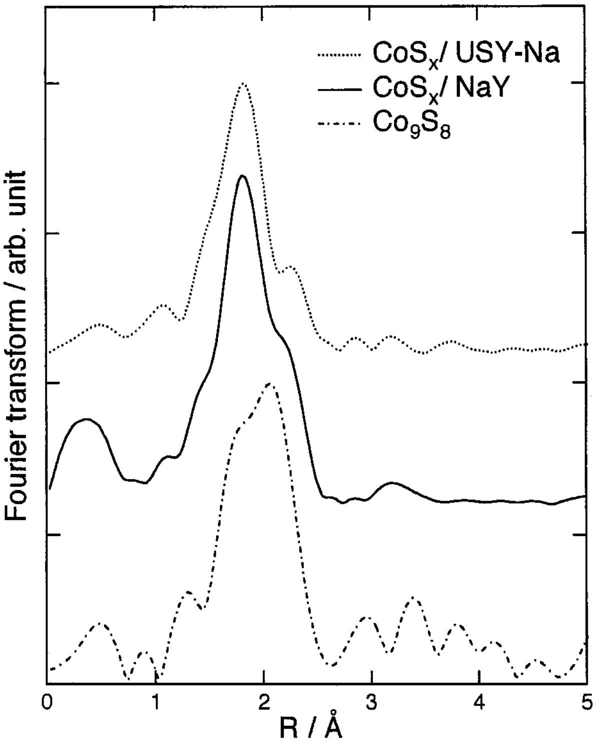

Figure 2. Fourier transforms of k^3-weighted Co K-edge EXAFS oscillation functions for CoS_x/USY-Na, CoS_x/NaY and Co_9S_8 ($\Delta k = 3.0$–15.0 $Å^{-1}$).

The amounts of NO adsorption on CoS_x/zeolite and the catalysts prepared by impregnation are presented in table 1. The catalysts prepared by the CVD technique, in particular CoS_x/USY-Na, show much higher NO adsorption capacities and, accordingly, higher dispersion of Co sulfide clusters than the impregnation catalysts. The thiophene HDS activity per adsorbed NO molecules (TOF) is compared in figure 3 for the Co sulfide catalysts. It is obvious from figure 3 that the CoS_x/USY-Na catalyst shows a much higher TOF than the other Co sulfide catalysts. These results indicate that the very high HDS activity of CoS_x/USY-Na is not only due to the increased number of active sites, but also due to the enhanced HDS activity of the surface Co atoms. Vissers et al. [9] reported that the inverse of the HDS activity (TOF based on Co) increases linearly with the Co loading for Co sulfide catalysts supported on activated carbon. That is, the activity of the Co atom increases as the Co loading decreases. They concluded by extrapolating the linear line to a zero loading that the HDS activity of optimally or atomically dispersed Co sulfide species is seven-fold higher than that of molybdenum sulfide and close to that of atomically dispersed Co species decorating MoS_2 edges. In the present study, it is shown by the EXAFS and NO adsorption results that atomically dispersed Co sulfide species are prepared in USY-Na zeolite even at a high Co loading, 6 wt% Co. It is certainly confirmed that the highly dispersed Co sulfide species show a very high HDS activity. The origin of the improved HDS activity of the highly, possibly atomically, dispersed Co sulfide species in CoS_x/USY-Na is not clear at present, but it may be due to a favorite electronic state of the Co sulfides in an extremely high dispersion [20]. Mo sulfide catalysts prepared from $Mo(CO)_6$, MoS_x/USY-Na, showed moderate activities comparable with that of MoS_x/NaY, possibly negating a major contribution of mesopores in USY-Na to the remarkably increased HDS activity of CoS_x/USY-Na.

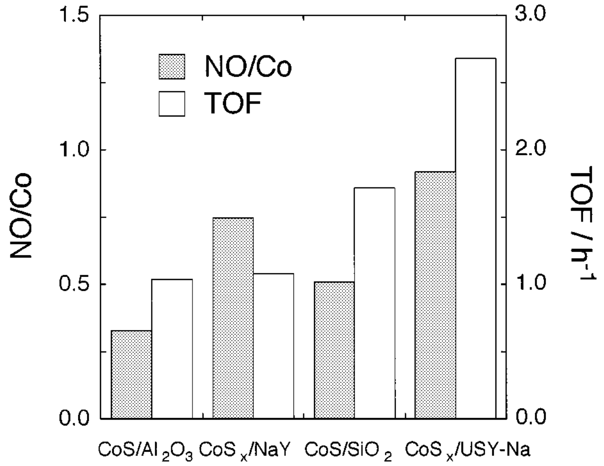

Figure 3. NO adsorption capacity and thiophene HDS activity per adsorbed NO molecules (TOF) for Co sulfide catalysts.

In summary, CoS_x/USY-Na catalysts are found to exhibit a much higher activity for thiophene HDS reaction than CoS_x/NaY and CoS–MoS_2/Al_2O_3. The loading and dispersion of Co sulfide clusters on CoS_x/zeolite catalysts are significantly affected by the Al/Si ratio of the host zeolite, when $Co(CO)_3(NO)$ is used as a precursor. The extremely high activity of CoS_x/USY-Na sulfide catalysts are attributed to the formation of atomically dispersed Co sulfide species.

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