A Novel Active Site Structure of Hydrodesulfurization Catalysts

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A novel structure of the CoMoS phase, dinuclear Co clusters located on the edges of MoS_2 particles, is proposed on the basis of an antiferromagnetic property of the Co atoms in highly active Co–Mo model sulfide catalysts prepared by a CVD technique using $Co(CO)_3NO$.

Hydrodesulfurization (HDS) catalysts have received increasing attention because of severer legislation towards cleaner fuels. Supported Mo or W sulfides promoted by Co or Ni have been the main catalytically active components in industrial catalysts.[1] Fundamental studies have been extensively conducted to elucidate the active phase in HDS catalysts. Topsøe and coworkers[1,2] proposed the so-called CoMoS phase as active sites in Co–Mo HDS catalysts on the basis of a variety of physicochemical characterizations, such as ^{57}Co Mössbauer emission spectroscopy, FTIR of NO adsorption and XPS. The CoMoS phase, in which Co atoms are located on the edges of finely dispersed MoS_2 particles, has been found to interpret many catalytic and spectroscopic aspects of Co(Ni)–Mo(W) sulfide catalysts.[1] The local structure of the CoMoS phase has been investigated by means of XAFS techniques. Bouwens et al.[3] and Niemann et al.[4] suggested that the Co(Ni) atoms constituting the CoMoS phase are isolated (no specific interactions between Co atoms) and are in a square pyramidal or octahedral configuration. Louwers and Prins[5] proposed a similar structure for the NiMoS phase, although they found a considerable Ni–Ni contribution in their EXAFS due to adjacent Ni atoms in a square pyramidal configuration. Thus, no specific interactions between the isolated Co or Ni atoms were assumed for the Co(Ni)MoS structure favorably accepted for more than a decade.

The magnetic property of Co sensitively reflects the chemical state of Co atoms and their mutual interactions. The magnetic property of the CoMoS phase has been studied by Topsøe et al.[6] with a conventional $Co–Mo/Al_2O_3$ impregnation catalyst and Co-promoted unsupported MoS_2 crystallites. With the impregnation catalyst, the CoMoS phase, Co^{2+} in Al_2O_3 and Co_9S_8 were simultaneously present and, hence, the accuracy of the magnetic moment of the CoMoS phase was considerably low, merely suggesting the presence of the interactions between Co atoms and MoS_2 particles. In the case of unsupported $Co–MoS_2$, no detailed analysis was conducted (effective magnetic moment of ca. 0.75 μ_B at 300 K). On the basis of the low effective magnetic moment, they concluded that the interaction of Co with MoS_2 edges caused electron delocalization and exchange effects. In the present study, we measured the magnetic susceptibility of Co atoms of highly active Co–Mo model sulfide catalysts, in which all the Co atoms form the CoMoS phase, to elucidate the structure of the CoMoS phase.

In the previous study,[7,8] we have shown that the CoMoS phase is selectively prepared by exposing supported MoS_2 catalysts to $Co(CO)_3NO$ vapor by a CVD technique (CVD-Co/MoS_2 model catalysts). The selective formation of the CoMoS phase was substantiated by XPS, Co K-edge XANES, NO adsorption, and HDS activity. The activity of CVD-Co/MoS_2/Al_2O_3 was much higher than that of conventional Co–Mo/Al_2O_3 impregnation catalysts for the HDS of thiophene.[7,8] In the present study, we prepared CVD-Co/MoS_2/Al_2O_3 (8.7 wt % Mo) and CVD-Co/MoS_2/SiO_2 (6.7 wt % Mo) according to the CVD technique as described previously.[7,8] Briefly, supported MoS_2 catalysts were exposed to a vapor of $Co(CO)_3NO$ for 5 min at room temperature, followed by evacuation for 10 min to remove physisorbed $Co(CO)_3NO$ molecules and subsequent resulfidation at 673 K for 1.5 h in a 10% H_2S/H_2 flow. Sulfided Al_2O_3 was exposed to $Co(CO)_3NO$ vapor, instead of MoS_2/Al_2O_3, to prepare CVD-Co/Al_2O_3. The catalyst sample was fused into a glass ampoule for a magnetic measurement after evacuation at 673 K for 1 h. The amount of Co anchored by the CVD technique was measured by using XRF. The catalytic results have been reported elsewhere.[7,8]

The static susceptibility measurement was done with a Faraday method using a Cahn 2000 Electro-Balance system at 4.2–300 K.[9] The effective magnetic moment and magnetic susceptibility were obtained by subtracting the magnetic contributions of the glass ampoule and MoS_2/Al_2O_3, MoS_2/SiO_2, or Al_2O_3 separately measured under the identical conditions.

Figure 1 shows the effective magnetic moment and magnetic susceptibility of Co for CVD-Co/MoS_2/Al_2O_3 (3.18 wt % Co) as a function of temperature. With decreasing temperature, the magnetic susceptibility χ of Co increased and had a sharp maximum at 16 K, followed by an abrupt decrease at a lower temperature. This temperature-dependency of χ is a typical antiferromagnetic behavior, clearly demonstrating that there are antiferromagnetic interactions between Co atoms forming the CoMoS phase. It seems difficult to explain the antiferromagnetism of the CoMoS phase on the basis of the structural models previously reported[3–5] on the basis of EXAFS analysis, since the Co^{2+} ($3d^7$) atoms in the models are isolated and expected to be paramagnetic in nature. Instead, we consider a model in which Co sulfide clusters are located on the edges of MoS_2 particles forming a one dimensional array. The antiferromagnetism with the temperature dependency of χ as observed in Figure 1 generates only when even numbered Co atoms are interacting. The smallest unit of such a structure is a dinuclear "compound" on the edges of MoS_2 particles. When we assume the formation of the dinuclear unit of two Co atoms (a spin pair model), the magnetic susceptibility χ of Co can be expressed by the following equation.[10]

$$\chi = \alpha N_A g^2 \mu_B{}^2 / k_B T [3 + \exp(-2J/k_B T)]$$

where N_A is Avogadro's constant, μ_B Bohr magneton, g gyromagnetic factor (assumed to be 2, here), k_B Boltzman's constant, J magnetic interaction strength defined by $H = -2JS_1 \cdot S_2$ (H; Hamiltonian) and α the fraction of the paramagnetic spin per

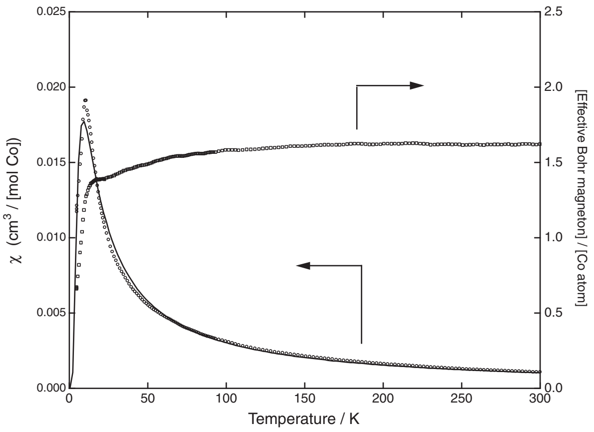

Figure 1. Magnetic susceptibility χ and effective magnetic moment (μ_B) of Co for CVD-Co/MoS_2/Al_2O_3 as a function of temperature. The best fitting curve, assuming a dinuclear cluster, for the observed magnetic susceptibility is also shown.

Co atom. It was found that the temperature dependency of the observed χ was rationally fitted ($J = -7.1\,K$, $\alpha = 0.84$) by using the theoretical equation as shown in Figure 1, indicating that the structure of the CoMoS phase is represented as Co dinucler clusters. It would also be possible to assume a larger size of 1-D clusters with even numbered Co atoms. However, the size of MoS_2 particles was 2–4 nm by TEM observations. Hence, it is reasonable to assume a dinuclear cluster as a unit as schematically illustrated in Figure 2. This structure is in excellent agreement with the one suggested by Raybaud et al.[11] on the basis of the DFT calculations at the full coverage of Co on the edges of MoS_2 particles. It has been shown that the edges of MoS_2 particles are fully occupied by Co atoms in the Co–Mo model catalysts prepared by using $Co(CO)_3NO$.[7,8]

When CVD-Co/MoS_2/Al_2O_3 was treated in a flow of H_2 (1 atm) at 673 K for 30 min, the antiferromagnetic behavior was not changed ($J = -6.9$ K, $\alpha = 0.96$) and no formation of paramagnetic species was detected. This finding suggests that the structure in Figure 2 is stable under HDS conditions (1 atm).

CVD-Co/MoS_2/SiO_2 (1.35 wt % Co) showed a similar temperature dependency of χ to that of the Al_2O_3-supported counterpart (Figure 1). The fitted parameters were $J = -8.5$ K and $\alpha = 1.2$. The interaction strength between the Co atoms is very close to that for CVD-Co/MoS_2/Al_2O_3. In the case of CVD-Co/Al_2O_3, the values of J and α were -7.5 K and 0.31, respectively, indicating a minor part of Co atoms form dinuclear compounds on the Al_2O_3 surface, although 70% of Co is present as a diamagnetic compound (Co_9S_8). It is also confirmed by means of the magnetic measurements that the present CVD technique is very effective to prepare selectively the CoMoS phase ($\alpha =$ 0.84–1.2).

In our previous study,[12] the amount of NO adsorption was measured for CVD-Co/MoS_2/Al_2O_3 and CVD-Co/MoS_2/SiO_2. It was found that only a half of Co atoms constituting the CoMoS phase can adsorb NO as a dinitrosyl form. It is difficult to interpret the NO adsorption property on the basis of the isolated Co sites, the CoMoS structure widely accepted at present.[3–5] However, the structure proposed in Figure 2 can easily explain the peculiar adsorption behavior of NO molecules on the CoMoS phase, assuming that one of the Co–S bonds is cleaved in a concerted manner when NO molecules approach to the site. Furthermore, the structure in Figure 2 is compatible with the EXAFS results published so far by several groups.[3–5] In particular, the structural parameters reported by Louwers and Prins[5] for the NiMoS phase are consistent with the structure in Figure 2, that is, the coordination number of Ni–Ni contribution at 0.32 nm is about 1.

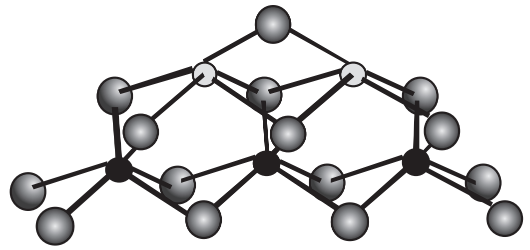

Figure 2. A schematic CoMoS structure. Small gray balls, Co atoms; Small black balls, Mo atoms; Large gray balls, S atoms.

It is shown, for the first time, from the magnetic study with the model Co–Mo sulfide catalysts that the structure of the CoMoS phase is described as dinuclear Co clusters on the edges of MoS_2 particles. The proposed dinuclear Co cluster model can explain the peculiar NO adsorption results.[12] The present results suggest that the structure in Figure 2 is thermally stable under working conditions as actual active sites.

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