Thermal Stability of Al_2O_3-supported Co–Mo–S Active Sites: Real Thermal Stability Separated from Sintering of MoS_2 Particles

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Real thermal stability of Al_2O_3-supported Co–Mo–S active sites was investigated, for the first time, separately from the sintering effect, showing that the Co–Mo–S structure is unstable to thermal treatments at 673 K and remarkably destroyed at 773 K, regardless of the presence of H_2S/H_2.

Continuing tightening of the sulfur content in transportation fuels has resulted in an increasing need for the development of highly active and selective hydrodesulfurization (HDS) catalysts.[1] Extensive research has been carried out on the Al_2O_3-supported Co(Ni)–Mo(W) hydrotreating catalysts, but the exact nature of the active sites and reaction mechanism thereon are still subjects of debate.[2,3] Topsøe and co-workers[2] have proposed that the catalytically active sites in the promoted catalysts are the so-called Co(Ni)–Mo–S phase (structure), in which Co(Ni) atoms are located on the edge of MoS_2 particles.

Deactivation of HDS catalysts during commercial operations is a crucial issue in industry. The main causes of the catalyst activity loss have been reported,[4] for example: active site poisoning by strongly adsorbed species, active site coverage by deposits (coke or metal), sintering of the active phase, and pore mouth blockage. The stability of the active phase is believed to contribute to the loss of HDS catalyst activity.[4] However, this issue has never been properly investigated, because of a difficulty to separate thermal decomposition of the active phase from degradation of the active phase due to the sintering of MoS_2 particles. In the present study, we can separate, for the first time, the sintering of MoS_2 particles from the decomposition of the Co–Mo–S phase by applying a CVD technique, by which Co promoter atoms are introduced after the formation of MoS_2 particles to minimize the structural change of the previously formed MoS_2 particles. For the purpose, the presulfidation of a MoS_2 catalyst is carried out at a high temperature for prolonged time to assure the formation of stable sintered MoS_2 particles. After Co atoms are introduced by the CVD technique, the resultant Co–Mo catalyst is sulfided again at a temperature lower than the presulfidation temperature to avoid a further sintering of the MoS_2 particles. A catalytic activity decrease with increasing sulfidation time of the Co–Mo catalyst, therefore, should be correlated only to the decomposition of the Co–Mo–S structure. To avoid the ambiguity caused by the deactivation of the catalyst due to coke formations, the thermal stability of the Co–Mo–S phase was studied between 473 and 873 K in a stream of H_2S/H_2 instead of during HDS reaction, assuming that both treatments essentially have the same effects on the stability of the phase.

In the present study, we prepared a MoO_3/Al_2O_3 catalyst (Mo content: 13 wt % MoO_3) by an impregnation technique, using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as a precursor. The catalyst was presulfided at 873 K for 4 h in a 10% H_2S/H_2 flow. Cobalt was introduced to the catalyst by a CVD technique.[5] Briefly, after evacuation at 673 K for 1 h, the catalyst was exposed at room temperature to a vapor of $Co(CO)_3NO$, and then evacuated at room temperature. Thereafter, the catalyst was sulfided in a similar manner, but the sulfidation temperature was varied at 473, 573, 623, 673, 773, or 873 K for 1.5 h. A prolonged sulfidation time up to 12 h was also used for the catalysts sulfided at 573, 673, and 773 K. The catalysts thus prepared are designated CVD-$Co/MoS_2/Al_2O_3$ followed by the second sulfidation temperature in parentheses, if necessary. The amount of Co incorporated by the CVD technique was determined by means of XRF. The catalyst activity test for the HDS of thiophene was performed at 623 K using a circulation reaction system made of glass, after an evacuation at 673 K for 1 h.[5]

Figure 1 depicts the HDS activity of CVD-$Co/MoS_2/Al_2O_3$ as a function of the second sulfidation temperature. The HDS activity was kept constant as the sulfidation temperature increased from 473 to 573 K then gradually decreased as the sulfidation temperature increased up to 673 K, followed by a more steep activity loss above 773 K. A thermal treatment of CVD-$Co/MoS_2/Al_2O_3$ in the absence of H_2S/H_2 (evacuation at $<10^{-3}$ Pa at a varied temperature) was also performed (data are not shown for brevity), showing that the HDS activity decreased with increasing evacuation temperature, in a way similar to that in the presence of H_2S/H_2.

Figure 2 shows the HDS activity of CVD-$Co/MoS_2/Al_2O_3$ as a function of sulfidation time. The HDS activity of CVD-$Co/MoS_2/Al_2O_3$(573) was kept constant as the sulfidation time was prolonged up to 12 h, while the HDS activity of CVD-$Co/MoS_2/Al_2O_3$(673) was gradually decreased with the sulfidation time. This result suggests that the Co–Mo–S structure is stable at 573 K, whereas it is slightly decomposed or unstable at 673 K. As for CVD-$Co/MoS_2/Al_2O_3$(773), the HDS activity was drastically decreased at the first 2 h treatment, followed by a gradual decrease with the treatment time, indicating that the Co–Mo–S structure is remarkably destroyed at 773 K. To confirm that the sintering of MoS_2 particles is not the cause of the decrease in the HDS activity, especially for CVD-$Co/MoS_2/Al_2O_3$(773), the following experiments were conducted: the fresh catalyst was first presulfided at 873 K for 4 h (the presulfidation condition used in the present study), subsequently the temperature was decreased to 773 K and the presulfidation was continued for another 5 h. After Co atoms were introduced by the CVD technique, the catalyst was sulfided at 673 K. The Co loading and the catalytic activity were compared to those of CVD-$Co/MoS_2/Al_2O_3$(673). The Co loading (Co: 1.70 wt %) and the HDS activity (Figure 1) were identical to those of CVD-$Co/MoS_2/Al_2O_3$(673) (Co: 1.66 wt %). Since the amount of Co atoms anchored by the CVD technique is proportional to the

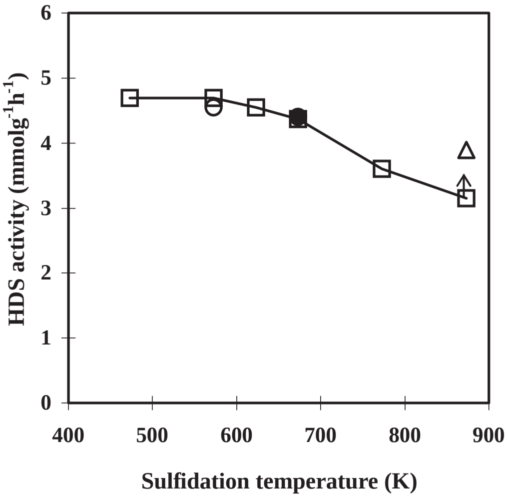

Figure 1. HDS activity as a function of the second sulfidation temperature. (□) CVD-Co/MoS_2/Al_2O_3, (△) double-CVD-Co/MoS_2/Al_2O_3(873,573), (○) double-CVD-Co/MoS_2/Al_2O_3(573,573), and (●) CVD-Co/MoS_2/Al_2O_3(673) presulfided at 873 K for 4 h then 773 K for another 5 h.

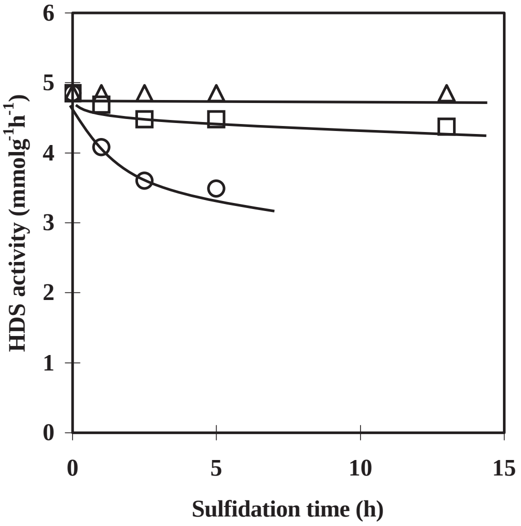

Figure 2. HDS activity as a function of sulfidation time. (○) sulfided at 773 K, (□) sulfided at 673 K, and (△) sulfided at 573 K.

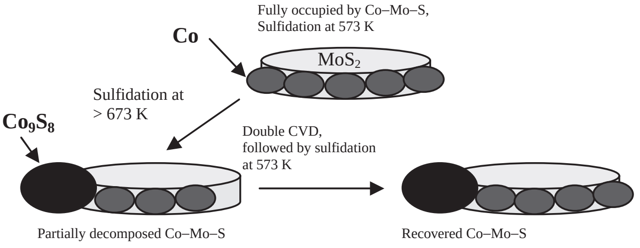

Figure 3. A degradation model of the Co–Mo–S structure.

edge dispersion of MoS_2 particles,[6] the same Co loading shows that no further sintering of MoS_2 particles takes place during the second sulfidation, even at 773 K for 5 h.

On the basis of the above results, we summarize the effect of the sulfidation at a high temperature on the Co–Mo–S structure as shown in Figure 3. The Co–Mo–S active sites present at 573 K is fully formed on the edge of MoS_2 particles.[5] This was confirmed by introducing Co atoms twice by the CVD technique to CVD-Co/MoS_2/Al_2O_3(573), followed by sulfidation at 573 K (denoted double-CVD-Co/MoS_2/Al_2O_3(573,573)). The HDS activity of double CVD-Co/MoS_2/Al_2O_3(573,573) was identical, within an accuracy, to that of CVD-Co/MoS_2/Al_2O_3(573) (Figure 1), indicating that all of the MoS_2 edge sites have been fully occupied by Co atoms by the first exposure to $Co(CO)_3NO$ vapor.[5,7] As for the Co–Mo–S structure treated above 673 K, a part of Co atoms is detached from the Co–Mo–S structure, leaving the MoS_2 edge sites vacant. The detached Co atoms are supposed to form catalytically inactive Co_9S_8 clusters. In order to confirm the formation of vacant edge sites of MoS_2 particles, Co atoms were introduced again by the CVD technique to CVD-Co/MoS_2/Al_2O_3(873), followed by a sulfidation at 573 K (double-CVD-Co/MoS_2/Al_2O_3(873,573)). The HDS activity of double-CVD-Co/MoS_2/Al_2O_3(873,573) became higher than that of CVD-Co/MoS_2/Al_2O_3(873) (Figure 1), indicating that some of the vacant MoS_2 edge sites in CVD-Co/MoS_2/Al_2O_3(873) was reoccupied by Co atoms present as the Co–Mo–S phase.[7] However, the activity recovery is only ca. 50% with respect to CVD-Co/MoS_2/Al_2O_3(573), the highest catalytic activity (Figure 1), indicating that ca. 50% of the MoS_2 edge sites have been blocked by Co_9S_8 clusters concomitantly formed during the second sulfidation at 873 K.

It is unambiguously concluded, for the first time, separating from the sintering effect that the Co–Mo–S structure is thermally stable at 573 K but unstable at 673 K. The Co–Mo–S structure was significantly destroyed at 773 K.

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References

1 C. Song, *Catal. Today*, **86**, 211 (2003).
2 H. Topsøe, B. S. Clausen, and F. E. Massoth, "Catalysis Science and Technology," ed. by J. R. Anderson and M. Boudard, Springer, Berlin (1996), Vol. 11.
3 D. D. Whitehurst, T. Ishoda, and I. Mochida, *Adv. Catal.*, **42**, 345 (1998).
4 E. Furimsky and F. E. Massoth, *Catal. Today*, **52**, 381 (1999).
5 Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, and T. Kubota, *Appl. Catal., A*, **226**, 115 (2002).
6 T. Kubota, K. Sato, A. Kato, Usman, T. Ebihara, T. Fujikawa, Y. Araki, K. Ishida, and Y. Okamoto, *Appl. Catal., A*, **290**, 17 (2005).
7 a) Y. Okamoto, K. Ochiai, M. Kawano, and T. Kubota, *J. Catal.*, **222**, 143 (2004). b) Y. Okamoto and T. Kubota, *Catal. Today*, **86**, 31 (2003).

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