Co–WS_2 Hydrodesulfurization Catalysts: An Unexpected More Favorable Combination than Co–MoS_2

Yasuaki Okamoto,* Akira Kato, Usman, Kenji Sato, and Takeshi Kubota
Department of Material Science, Shimane University, Matsue 690-8504

(Received June 14, 2005; CL-050763)

The specific activity of the Co–W–S phase, formed on WS_2/SiO_2 (presulfided above 973 K) by a CVD technique using $Co(CO)_3NO$, was 1.6 times as high as that of the Co–Mo–S phase formed on MoS_2/SiO_2 (above 873 K) for the hydrodesulfurization of thiophene, demonstrating, for the first time, that in sharp contrast to general belief, Co–WS_2 is a much more favorable combination for the generation of catalytic synergy than Co–MoS_2, which has been widely used in industry.

Development of highly active hydrodesulfurization (HDS) catalysts has been and is one of the most urgent issues in petroleum industry for protecting the environment.[1] Supported molybdenum sulfides promoted by Co or Ni have been extensively used in industry for HDS reaction.[2,3] Supported tungsten sulfide catalysts promoted by Ni have also been widely studied because of the generation of strong catalytic synergy between W and Ni. On the other hand, Co–W sulfide catalysts have received much less attention compared to the other three combinations owing to much weaker promotional effects of Co in conventionally prepared Co–W catalysts.[4,5] The reason of the weak catalytic synergy between cobalt and tungsten sulfides is, however, not clear enough at present.

The HDS activity of Co-promoted Mo or W catalysts is determined by the amount of active sites and their intrinsic activity. Topsøe and co-workers[3] have proposed that the catalytically active phase in Co–MoS_2 catalysts is the so called Co–Mo–S phase (structure), in which Co atoms are located on the edge of MoS_2 particles. To understand the nature of the inefficient Co–WS_2 combination, it is, therefore, strongly needed to compare the intrinsic activities of the Co–Mo–S phase and the Co–W–S phase for HDS reaction. Using the FTIR, NO adsorption,[6,7] Co2p XPS,[8] Co K-edge XANES,[9] and magnetic susceptibility,[7] we have shown that supported Co–Mo(W)S_2 catalysts, in which the edge of MoS_2 or WS_2 particles is selectively and fully occupied by Co atoms forming the Co–Mo(W)–S phase, can be prepared when presulfided Mo(W) catalysts are exposed to $Co(CO)_3NO$ vapor (CVD technique), followed by evacuation and resulfidation. The Co–Mo(W) catalysts thus prepared by the CVD technique are denoted CVD-Co/Mo(W)S_2/support here. It should be noted that the amount of Co atoms in the CVD-catalysts corresponds to the amount of the active sites.[8]

In the present study, we examined the effect of the presulfidation temperature (673–1173 K) on the intrinsic activity of the Co–Mo–S phase and the Co–W–S phase. It is unexpectedly demonstrated, for the first time, that a Co–WS_2 combination is much more favorable than a conventional Mo counterpart, which has been commercially used for more than 50 years.

10 wt % MoO_3/SiO_2 and 20 wt % WO_3/SiO_2 (SiO_2, 370 $m^2\,g^{-1}$) were prepared in an analogous way to the previous study.[8] The MoO_3/SiO_2 or WO_3/SiO_2 catalyst thus prepared was presulfided at 673–1173 K for 2 h in a 10% H_2S/H_2 flow at an atmospheric pressure. The Mo(W)S_2 catalyst is designated as Mo(W)S_2/SiO_2. Cobalt was introduced to MoS_2/SiO_2 and WS_2/SiO_2 by a CVD technique.[8] Briefly, MoS_2/SiO_2 was first evacuated at 673 K for 1 h and subsequently exposed at room temperature to a vapor of $Co(CO)_3NO$. After evacuation at room temperature, the sample was sulfided again at 673 K for 1.5 h to prepare CVD-Co/MoS_2/SiO_2 regardless of the presulfidation temperature of MoS_2/SiO_2. CVD-Co/WS_2/SiO_2 was also prepared in a similar manner. The amount of Co incorporated by the CVD technique was determined by means of XRF (Shimadzu EDX-700HS).

The initial activity of the freshly prepared catalyst for the HDS of thiophene was evaluated at 623 K using a circulation reaction system made of glass under mild reaction conditions (initial H_2 pressure, 20 kPa). The HDS activity was calculated on the basis of the accumulated amount of H_2S. The detailed reaction procedures have been reported previously.[8]

Figure 1 shows the HDS activity of CVD-Co/Mo(W)S_2/SiO_2 as a function of the presulfidation temperature of Mo(W)S_2/SiO_2. The activity increased as the presulfidation temperature was increased and then decreased after taking a maximum at 873 and 973 K for the Co–MoS_2 and Co–WS_2 catalysts, respectively, although the edge dispersion of the MoS_2 and WS_2 particles monotonously decreased as evidenced by the amount of NO adsorption on Mo(W)S_2/SiO_2 (not shown) and by the amount of Co (Co/Mo(W) mole ratio) accommodated in CVD-Co/Mo(W)S_2/SiO_2 (Figure 1). The surface area and pore size distribution of WS_2/SiO_2 were not varied by the presulfidation at 1073 K. Regardless of the presulfidation temperature (673–1173 K), there were proportional correlations between the Co/Mo(W) mole ratio of CVD-Co/Mo(W)S_2/SiO_2 and the NO/Mo(W) mole ratio of Mo(W)S_2/SiO_2, confirming that the Co atoms introduced by the CVD technique are selectively located on the edge of Mo(W)S_2 particles forming the Co–Mo(W)–S phase, in agreement with our previous study on CVD-Co/Mo(W)S_2/support catalysts.[8] This indicates that the Co-accommodation property of the edge of Mo(W)S_2 particles is not modified by the presulfidation temperature.

The turnover frequency (TOF) of the HDS of thiophene on the active sites, the Co–Mo(W)–S phase,[3] of the CVD-catalysts was calculated on the basis of the amount of Co in the catalyst. Figure 2 presents the TOF as a function of the presulfidation temperature of Mo(W)S_2/SiO_2. The TOF on the Co–Mo–S phase slightly increased as the temperature was increased and leveled off above 873 K, substantiating the transformation of moderately active sites formed at 673 K into highly active Co–Mo–S Type II.[3] This is totally consistent with the results by Topsøe et al.[3] showing by means of ^{57}Co Mössbauer emission

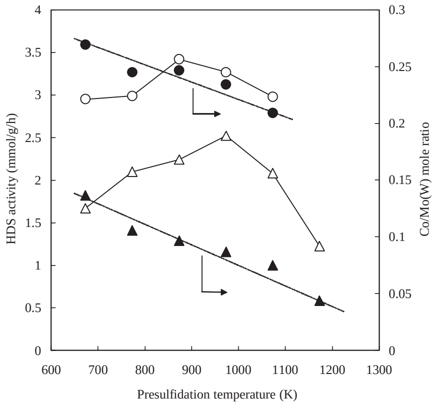

Figure 1. Catalytic activity of CVD-Co/MoS_2/SiO_2 (○) and CVD-Co/WS_2/SiO_2 (△) for the HDS of thiophene as a function of the presulfidation temperature. The amount of Co incorporated by the CVD technique is also shown (●, Co/Mo mole ratio and ▲, Co/W mole ratio).

spectroscopy that Co–Mo–S Type II is formed by the sulfidation of conventional Co–Mo/Al_2O_3 catalysts at above 875 K. However, the TOF on the Co–W–S phase increased more profoundly with increasing presulfidation temperature of WS_2/SiO_2 and leveled off above 973 K. In the analogy to the definition of Co–Mo–S Type II,[3] it is concluded that Co–W–S Type II can be formed only by the presulfidation above 973 K. The TOF on the Co–W–S phase remarkably exceeded that on the Co–Mo–S phase at the presulfidation temperature higher than 773 K. In particular, the TOF on Co–W–S Type II was 1.6 times as high as that of the Co–Mo–S Type II, demonstrating that in sharp contrast to general belief, Co–WS_2 is a much more favorable combination than Co–MoS_2 for the generation of catalytic synergy for HDS. The latter combination has been commercially employed for more than 50 years. Since the edges of MoS_2 and WS_2 particles are fully occupied by the Co atoms forming the Co–Mo(W)–S phase in the CVD-catalysts,[6–8] the lower HDS activity of CVD-Co/WS_2/SiO_2 in Figure 1 is apparently ascribed to a lower dispersion of WS_2 particles than that of MoS_2 particles, as evidenced by the lower amount of the Co atoms accommodated in the catalyst (Co/W $\ll$ Co/Mo). It is expected that Co–WS_2 catalysts could show higher HDS activity than Co–MoS_2 catalysts, if the former catalysts were properly prepared by a sophisticated manner.

It has been generally believed that the formation of Co–Mo–S Type II is attributed to complete sulfidation of Mo and the formation of stacked MoS_2 particles.[3] The sulfidation of Mo and W was completed at above 673 and 773 K, respectively, for the SiO_2-supported catalysts as evidenced by XANES.[5] When MoS_2/SiO_2 (673) presulfided at 673 K was evacuated at 873 K for 2 h prior to the admission of Co by the CVD technique, the TOF on CVD-Co/MoS_2/SiO_2 (673) significantly increased to the value observed for Co–Mo–S Type II, as shown in Figure 2. Therefore, the present results in Figure 2 clearly show that Co–Mo–S Type II is formed simply by a high temperature treatment (presulfidation or evacuation) of MoS_2 particles but not by a high temperature treatment of the Co–Mo–S phase, that is, Co–Mo–S Type II is readily formed even at a low temperature (673 K) on the edge of MoS_2 particles which had been subjected to a high temperature treatment (above 873 K for MoS_2). It may be speculated that the formation of Co–Mo(W)–S Type II is correlated to increased crystallinity of Mo(W)S_2 particles at a high temperature.

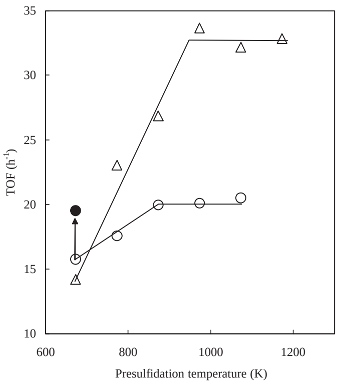

Figure 2. TOF on the Co–Mo–S phase (○) and the Co–W–S phase (△) as a function of the presulfidation temperature. ●, CVD-Co/MoS_2/SiO_2 in which MoS_2/SiO_2 had been presulfided at 673 K and subsequently evacuated at 873 K for 2 h.

This work was supported by Grant-in-Aid for Scientific Research (No. 16360404) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 C. Song, *Catal. Today*, **86**, 211 (2003).
2 R. Prins, in "Handbook of Heterogeneous Catalysis," ed. by G. Ertl, H. Knözinger, and H. J. Weitkamp, VCH, Weinheim (1997), p 1908.
3 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, p 1.
4 G. Kishan, L. Coulier, J. A. R. van Veen, and J. W. Niemantsverdriet, *J. Catal.*, **200**, 194 (2001).
5 T. Kubota, N. Hosomi, K. Bando, T. Matsui, and Y. Okamoto, *Phys. Chem. Chem. Phys.*, **5**, 4510 (2003).
6 Y. Okamoto and T. Kubota, *Catal. Today*, **86**, 31 (2003).
7 a) Y. Okamoto, M. Kawano, T. Kawabata, T. Kubota, and I. Hiromitsu, *J. Phys. Chem. B*, **109**, 288 (2005). b) Y. Okamoto, T. Kawabata, T. Kubota, and I. Hiromitsu, *Chem. Lett.*, **32**, 1150 (2003).
8 a) Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, and T. Kubota, *Appl. Catal., A*, **226**, 115 (2002). b) Y. Okamoto, A. Kato, Usman, K. Sato, I. Hiromitsu, and T. Kubota, *J. Catal.*, **233**, 16 (2005).
9 Y. Okamoto, K. Ochiai, M. Kawano, and T. Kubota, *J. Catal.*, **222**, 143 (2004).

Published on the web (Advance View) August 13, 2005; DOI 10.1246/cl.2005.1258