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THE FORM OF SULFIDE ON MOLYBDENUM OXIDE CATALYST

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Molybdenum oxide catalyst is sulfurized during the hydrodesulfurization reaction. The catalyst was studied by EMX and ESCA. Sulfur was mainly contained as MoS_2. Mo/S mole ratio of the catalyst was 1.5-3.4 by ESCA and 5.7 by chemical analysis. This means that sulfide is mainly distributed on the surface or near the surface.

When molybdenum oxide is used as a catalyst for hydrodesulfurization of thiophene, the catalyst is gradually sulfurized with the time of reaction and the sulfur content reaches a steady value.$^{1)}$ The author reported$^{2)}$ that the catalytic activity was affected by the sulfur contents of the catalyst. The sulfur has been confirmed to be contained as MoS_2 when the sulfur contents are large enough,$^{3)}$ but there is no evidence of the formation of MoS_2 when the sulfur content is small.$^{1,4)}$ The author tried to detect the sulfide in the catalyst at the steady stage of the reaction by a X-ray diffraction analysis, but did not obtain a successful result, probably because the sulfur content(350°C;46.7mg, 375°C;42.7mg, 400°C;28.3mg) was too small, or because the sulfide was amorphous or very small particles.$^{1)}$

The author studied the form of the sulfide by electron microprobe X-ray analysis (EMX) and electron spectroscopy for chemical

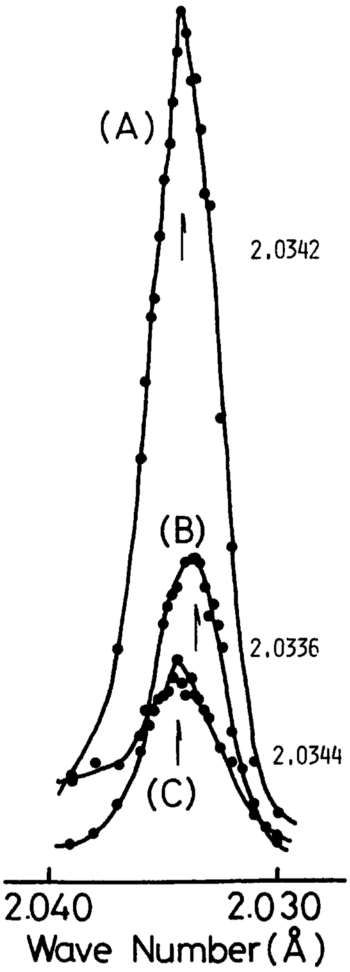

Fig. 1. S Kα spectra of MoS_2(A), pure sulfur(B) and the catalyst sample(C).

analysis(ESCA). According to EMX with S Kα radiation, the sulfur was distributed all over the catalyst, showing that the catalyst was sulfurized uniformly, as reported previously.[5] It is well known[6,7] that the peak of the spectrum of soft X-ray radiation shifts according to the form of chemical bond. Figure 1 shows the spectra of soft X-ray radiation of S Kα of MoS_2 powder(A), pure sulfur powder (B), and the catalyst(used at 350°C for 60 min), bomberded with electron of 8 KV. The peak of S Kα line of the catalyst(2.0344 Å) agrees well with that of MoS_2(2.0342 Å) and differs from that of pure sulfur(2.0366 Å). Although the resolution is not so good, the chemical shift is detectable, showing that the catalyst contains sulfur as sulfide.

ESCA(HITACHI spectrometer) was used to obtain more precise information on the form of the sulfide in the catalyst. The samples were exposed to X-ray radiation from magnesium anode bomberded with electron of 11 KV. The values obtained are refered to C(1s). The binding energies(BE) were calculated from the equation, BE=hν-KE-ψ-RE, where hν is the energy of Mg Kα(1253.6 eV), KE, kinetic energy (observed values), ψ, work function of the spectrometer(4.75 eV) and RE, recoil energy (~0 eV).

Figure 2, 3 and 4 show the ESCA spectra of the catalyst(A) and MoS_2(B). Figure 2 shows Mo 3p spectra. The shoulder is observed at the KE of 854.0 eV in the spectrum(A). This agrees well with that of MoS_2(B). The main peak(KE= 849.8 eV) of the spectrum(A) was somewhat

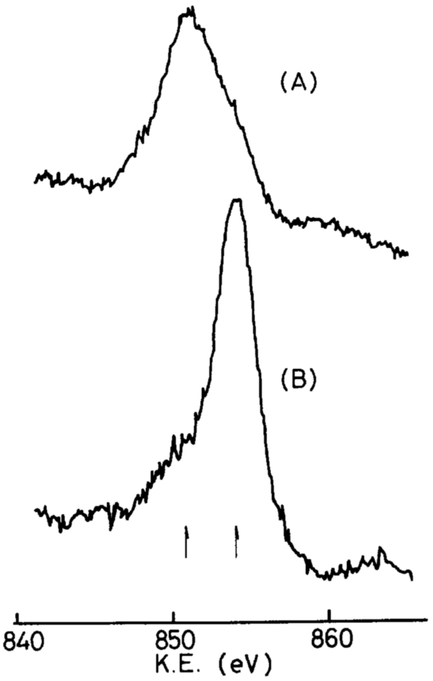

Fig. 2. Mo 3p ESCA spectra of the catalyst sample(A) and MoS_2(B).

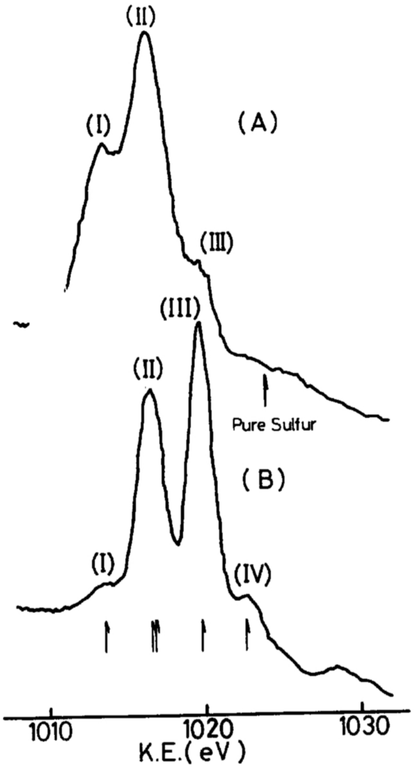

Fig. 3a. Mo 3d and S 2s ESCA spectra of the catalyst sample(A) MoS_2(B).

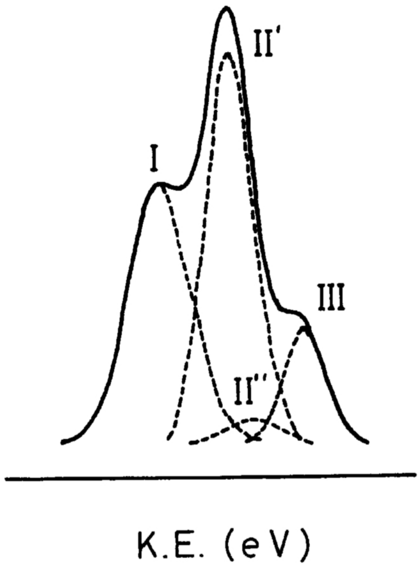

Fig. 3b. Analysis of Mo 3d spectrum of the catalyst sample.

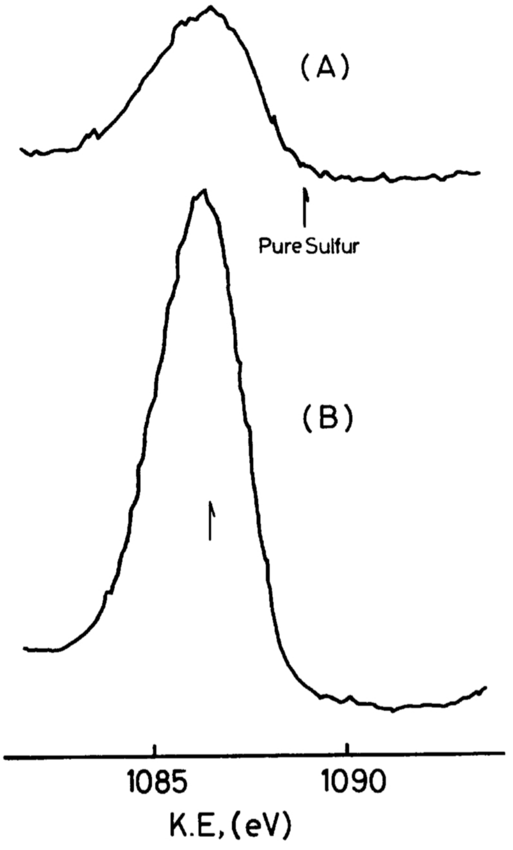

Fig. 4. S 2p ESCA spectra of the catalyst sample(A) and MoS_2(B).

lower than the reported value for MoO_2,[8)] but, according to X-ray diffraction analysis, the catalyst was reduced to MoO_2 during the reaction.[9)] Figure 3a shows Mo 3d and S 2s spectra. Mo 3d spectrum of MoS_2 has two peaks II (KE=1016.1 eV) and III(1019.8 eV) which correspond to Mo $3d_{3/2}$ and $3d_{5/2}$ of MoS_2, respectively. Three distinct peaks are observed for the catalyst(A). This spectrum is analysed by a curve resolver as shown in Fig. 3b. According to the curve resolver, the peak II is divided into two peaks, II' and II''. The peaks I(KE=1013.4 eV) and II'(1016.6 eV) are due to Mo $3d_{3/2}$ and $3d_{5/2}$ of molybdenum oxide. The peaks II''(1016.1 eV) and III(1019.6 eV) agree with peaks II and III of the spectrum(B) and are due to Mo $3d_{3/2}$ and $3d_{5/2}$ of MoS_2. The peak IV of the spectrum(B) in Fig. 3a is due to S 2s of MoS_2, which differs from that of free sulfur(marked with arrow). The peak IV of the catalyst(A) is negligible small.

Figure 4 shows S 2p spectra. The BE of sulfur of the catalyst is 161.6 eV(KE=1087.3 eV) and that of MoS_2 is 161.8(1087.1 eV). These values differ from that of free sulfur (BE=160.1 eV, KE=1088.8 eV, marked with arrow). The values are also close to the value of MoS_2 obtained by other workers.[8,10)] The half width of S 2p spectrum of the catalyst(3.15 eV) is larger, compared with that of MoS_2(2.70 eV). This suggests that the catalyst contains not only MoS_2 but also some other forms of the sulfide.

Mo/S mole ratios of the catalyst and MoS_2

powder, obtained by ESCA, are 1.5-3.4 and 0.6-0.7, respectively. Mo/S mole ratio of the catalyst calculated by chemical analysis was 5.7, and theoretical ratio of MoS_2 is 0.5. It is well known$^{11)}$ that ESCA gives an information of composition of the surface or of the thin surface layer. Accordingly, these results indicate that the sulfide mainly distributes on the surface or near the surface of the catalyst.

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References

1) N. Sotani and M. Hasegawa, Bull. Chem. Soc. Jap., 46, 25(1973).
2) N. Sotani, Rev. Phys. Chem. Soc. Japan, 46, 9(1976).
3) K. S. Seshadri, F. E. Massoth, and L. Petrakis, J. Catal., 19, 95(1970).
4) S. Namba and T. Aonuma, Kogyo Kagaku Zasshi, 74, 1324(1971).
5) N. Sotani and M. Hasegawa, Chem. Lett., 1975, 1309.
6) A. J. McAlister, R. C. Dobbyn, J. R. Cuthill, and M. L. Williams, J. Phys. Chem. Ref. Data., 2, 411(1973).
7) S. J. B. Reed,'' Electron Microprobe Analysis,'' Cambridge University Press, London(1975), 319.
8) T. A. Patterson, J. C. Caxver, D. E. Leyden, and D. M. Hercules, J. Phys. Chem., 80, 1700(1976).
9) N. Sotani, Bull. Chem. Soc. Jap., 48, 1820(1975).
10) G. C. Stevens and T. Edmonds, J. Catal., 37, 544(1975).
11) Y. Baer, P. F. Hedén, J. Hedman, M. Klasson, C. Nordling, and K. Siebahn, Physica Script., 1, 55(1970).

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