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SURFACE STATE AND CATALYTIC ACTIVITY OF MoO_3/Al_2O_3 CATALYST IN THE HYDRODESULFURIZATION OF THIOPHENE STUDIED WITH X-RAY PHOTOELECTRON SPECTROSCOPY

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The surface states of MoO_3/Al_2O_3 catalysts used for the hydrodesulfurization of thiophene were characterized with XPS and compared with the activities for the reaction. It was found that the molybdenum with a stoichiometry of S/Mo(IV)=1 is much more active than MoS_2, indicating the importance of an anion vacancy for the reaction.

The structures of oxidic MoO_3/Al_2O_3 catalysts have been studied extensively and characterized well by using various phisico-chemical techniques (1-4). However, the structures of MoO_3/Al_2O_3 catalysts sulfided by presulfidation and hydrodesulfurization (HDS) reaction of sulfur compounds remain equivocal particularly when MoO_3 is partially sulfided. In our previous papers (5,6), the sulfided species having a composition of S/Mo(IV)=1 has been proposed to be more active than MoS_2 for the HDS reaction of thiophene, based on XPS results under mild reaction conditions (10 Torr of thiophene/H_2). However, the validity of proposed species for usual reaction conditions employed by many workers seems somewhat ambiguous because of large differences in the reaction conditions among them (6,7). Therefore, it would be interesting to characterize the surface states of MoO_3/Al_2O_3 catalysts sulfided under atmospheric pressure of thiophene/H_2 conditions and to elucidate active species for the reaction.

MoO_3/Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 with ammonium paramolybdate, drying at 100°C, and calcining at 550 or 700°C for 5 hr. The amounts of supported MoO_3 were 4.8, 9.1, 13.0, 16.7, and 23.1 wt% and the surface areas were 168, 167, 156, 147, and 122 m^2/g for the catalysts calcined at 550°C and 135, 122, 67, 62, and 58 m^2/g for the 700°C calcined catalysts, respectively.

The HDS reaction of thiophene was undertaken over the MoO_3/Al_2O_3 catalyst at 400°C under an atmospheric pressure of thiophene/H_2 (1/18, H_2 flow rate; 50 ml/min) using a fixed bed flow reactor. The catalyst was subjected to one of the following pretreatments prior to the reaction; 1) prereduction at 400°C for 1 hr with H_2 (50 ml/min), 2) presulfidation at 400°C for 1 hr with CS_2/H_2 (1/9, H_2; 27 ml/min), and 3) no-pretreatment where thiophene/H_2 was fed directly over the oxidic catalyst. Diffusion effects on the conversion of thiophene were eliminated by choosing appropriate reaction conditions. The conversions of thiophene were measured within an accuracy of $\pm$ 1%. The catalyst sample was removed from the reactor without exposing it to air or moisture after reaching the steady state conversion and, subsequently, cooling the sample to room temperature in a N_2 stream. The catalyst was transferred to a N_2-filled dry box attached to a XPS pretreatment chamber. The XPS spectra were measured at room temperature on a Hitachi 507 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation as described previously in detail (8). The catalyst powder was mounted on a double-sided adhesive tape. The S/Mo atomic ratios were calculated from the S 2p/Mo 3d XPS area intensity ratios calibrated by using MoS_2 (5). The accuracy of S/Mo ratio thus obtained was estimated to be ± 3%.

The intrinsic activity of MoO_3 (conversion/unit MoO_3) for the HDS reaction of thiophene is plotted in Fig.1 as a function of the sulfidation degree of molybdenum (S/Mo). A volcano-type relation was apparently obtained. It is worth noting that the intrinsic activity of MoO_3 depends on the degree of sulfidation of molybdenum alone, regardless of the pretreatment conditions, MoO_3 content, and calcination temperature of the catalyst. Taking into account the fraction of Mo(IV) (Mo $3d_{5/2}$; 229.3 eV where Al 2s; 119.6 eV) in the molybdenum, the S/Mo ratios on the left side of the volcano-type curve resulted in S/Mo(IV)=1. Therefore, it is concluded that S/Mo(IV)=1 species is present on the catalyst surface as well as MoS_2 and that it shows much higher intrinsic activity for the HDS reaction than MoS_2, as suggested previously (5). From Fig.1 it is evident that S/Mo(IV)=1 species is produced only when MoO_3 content is low and the catalyst is not subjected to severe sulfidation conditions such as the presulfidation.

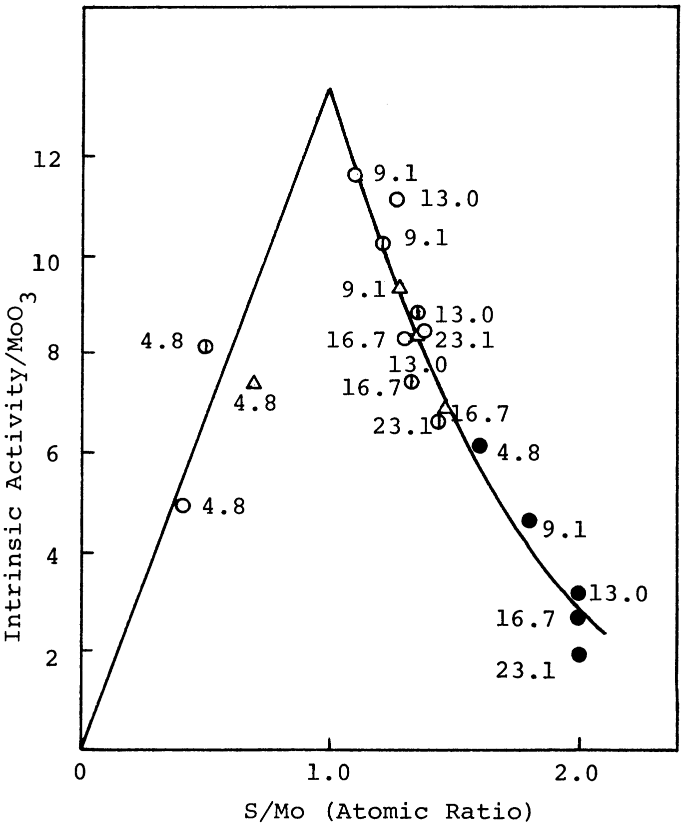

Fig.1 Correlation between the intrinsic activity for the HDS reaction of thiophene and the degree of sulfidation of Mo. ○ , △;H_2 prereduction, ⦶ ; no-pretreatment, ● ;presulfidation: circle; catalyst calcined at 550°C, triangle; at 700°C. The numbers in Figure indicate MoO_3 content (wt%).

In order to characterize the structure of the active molybdenum, pyridine adsorption experiments were carried out using a pulse technique with a catalyst (13 wt% MoO_3, calcined at 550°C) sulfided at 400°C to various extents with CS_2 pulses in a H_2 stream. The amounts of adsorbed pyridine were measured at 150°C in a He stream. It is well known that pyridine poison effectively the HDS reaction (9,10). It is reasonable to assume that the amount of pyridine retained on the catalyst corre-

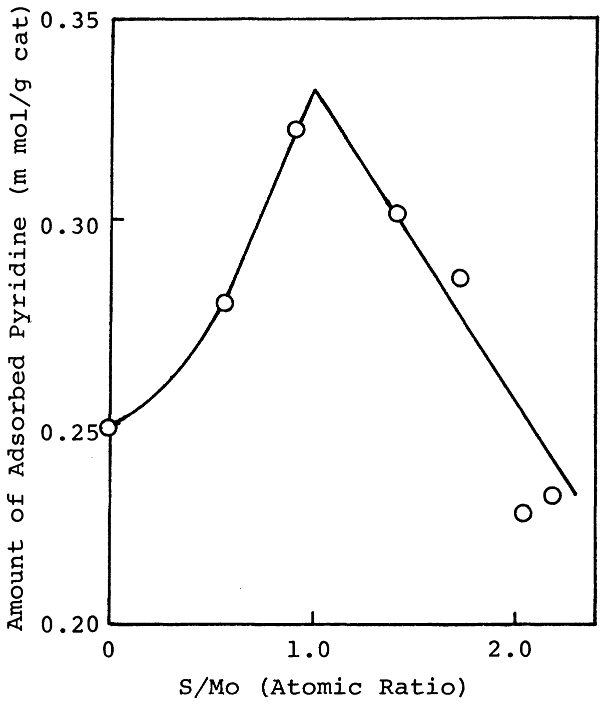

Fig.2 Dependence of the amount of adsorbed pyridine upon the sulfidation degree of Mo. catalyst; 13 wt% MoO_3, calcined at 550°C, adsorption temperature; 150°C.

lates to the amount of active site for the HDS reaction or to the concentration of a vacancy on molybdenum (9), although the adsorbed pyridine observed here would contain some pyridine adsorbed on the bare surface of alumina. Figure 2 shows the amount of adsorbed pyridine as a function of S/Mo ratio. It is noteworthy that a maximum is observed again for the catalyst with the composition of S/Mo=1. Combining the results in Figs.1 and 2, it is supposed that S/Mo(IV)=1 species contains the largest amount of anion vacancy in it. Accordingly, it is considered that the active species with a stoichiometry of S/Mo(IV)=1 is attributed to **1** in Fig.3, which has an analogous structure to well-defined **2** (3,4,11). This is supported by the findings that **1** is observed preferentially only in the low MoO_3 content catalysts and that it is not stable for severe sulfidation, since molybdenum in tetrahedral surroundings, which is considered to be a main precursor of **1**, is present on the catalyst containing a small amount of MoO_3 (1,2).

A plausible reaction mechanism of the HDS reaction of thiophene involving redox cycle of Mo(IV) and Mo(VI) and **1** as an active species is proposed in Fig.3. Contrary to the mechanism suggested by Lipsch and Schuit (12), this mechanism involves hetero-

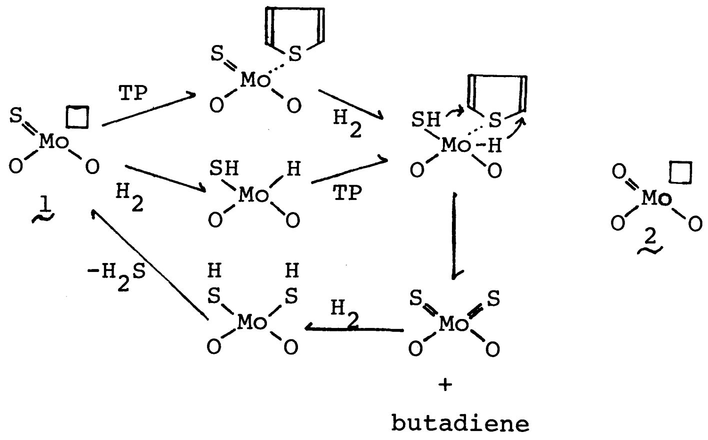

Fig.3 Possible HDS reaction mechanism of thiophene (TP) on **1**

lytic adsorption of hydrogen on a sulfur anion and a vacancy, which type of hydrogen is supposed to be reversibly adsorbed (13) and to be active for the HDS reaction (14). As shown in Fig.2, MoS_2 does not contain so much vacancies as **1**. MoS_2 would have vacancies only in the edges and corners. Therefore, it is reasonable to explain the low activity of MoS_2 in terms of the vacancy concentration. This implys the importance of the vacancy on molybdenum in the HDS reaction (12,15).

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