

Effect of H<sub>2</sub>S on Hydrogenation Activity of Sulfided Co/Mo/Al<sub>2</sub>O<sub>3</sub>

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Effect of gas-phase H<sub>2</sub>S on the reactions of aromatic hydrocarbons over sulfided Co/Mo/Al<sub>2</sub>O<sub>3</sub> was studied at 400 °C. The added H<sub>2</sub>S inhibited hydrogenation of benzene but accelerated hydrogenation of o-xylene. No effect was exerted upon hydrogenation of toluene. At all instances, the added H<sub>2</sub>S accelerated skeletal isomerization.

Presulfided Co/Mo/Al<sub>2</sub>O<sub>3</sub> is currently used in heavy oil upgrading. Efforts are still being made, however, to improve its catalytic performance. One of these efforts is to modify sulfiding level of the surface layer of the presulfided catalyst by the concurrent introduction of H<sub>2</sub>S with the feed. Reported results appear, however, to be quite conflicting. The gas-phase H<sub>2</sub>S has been shown to promote hydrogenative reactions in a number of instances,<sup>1-3)</sup> but the contrary has also been reported frequently.<sup>4-6)</sup> We report, in the present paper, the effect of the gas-phase H<sub>2</sub>S on the reactions of benzene, toluene, and o-xylene over a presulfided Co/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. These compounds are chosen as probe substrate, since they are known to be not so reactive in hydrogenative reaction,<sup>7)</sup> and hence results are expected to reflect catalysts activity more clearly.

A conventional flow reactor was used. Three grams of a commercial Co/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (4.4 wt% CoO and 14.9 wt% MoO<sub>3</sub>) was placed in the reactor vessel. Prior to the test runs, the catalyst was presulfided with H<sub>2</sub>S(5%)/H<sub>2</sub>(95%) gas mixture of 1 MPa at 400 °C. Reactions were carried out at 400 °C and 5 MPa with LHSV 4.5 h<sup>-1</sup> and H<sub>2</sub>/Feed of 1000 vol/vol. Product compositions were determined by a gas chromatograph equipped with a 50 m OV-101 glass capillary column.

The products observed were as follows; cyclohexane and methylcyclopentane for benzene, methylcyclohexane and dimethyl-, ethyl-cyclopentane for toluene, dimethyl-cyclohexanes and dimethyl-ethyl-, trimethyl-cyclopentanes for o-xylene. Product-pattern observed here was similar each other and was considered to be caused by ring saturation and subsequent skeletal isomerization. Total conversion and the ratio(isomerization conversion/total conversion) were used as an index of hydrogenation activity and isomerization activity, respectively. Effect of H<sub>2</sub>S on hydrogenation activity was examined by adding H<sub>2</sub>S to H<sub>2</sub> flow in stepwise so as to be 5% by volume. As is shown in Fig.1, the added H<sub>2</sub>S brings about promotion and inhibition for o-xylene and benzene, respectively. No effect is found for hydrogenation of toluene. Concerning the isomerization activity, however, the added H<sub>2</sub>S brings about promotion for all three reactants.

The promotion effect of  $H_2S$  was furthermore investigated for hydrogenation of *o*-xylene. As is shown in Fig.2, coexisting  $H_2S$  clearly keeps the activity at higher level, and the degree of the promotion depends on  $H_2S$  concentration. Activity increases with increasing concentration of  $H_2S$  up to 5% and then decreases. The activity in  $H_2S(5\%)/H_2(95\%)$  is three times as high as that in  $H_2$  at time on stream of 7 hours. In other words, the added 5%  $H_2S$  increases twice the conversion in  $H_2$  atmosphere. Since the amount of hydrogen supplied from the added  $H_2S$  is much less than that of hydrogen incorporated into *o*-xylene, this increase of conversion is not attributed to Ha in the following reaction, in which  $H_2S$  dissociatively adsorbs to form active hydrogen (Ha) on catalyst surface.  $H_2S \rightarrow 2Ha + S$  (1). Thus the main role of  $H_2S$  is to modify the catalyst surface as follows.  $Mo + H_2S \rightleftharpoons H - Mo - SH \rightleftharpoons Mo - S + H_2$  (2). Here  $Mo - S$  is the newly formed active site. This formation results in the promotion effect. However,  $H_2S$  also functions to adsorb competitively with reactant on active site. If  $H_2S$  adsorbs more strongly than reactant (in the case of benzene) or  $H_2S$  concentration in the gas phase becomes higher (in the case of 10%  $H_2S$  for *o*-xylene), active sites are blocked by  $H_2S$ . This results in the inhibition effect. In the case of *o*-xylene, it adsorbs on active sites more strongly than  $H_2S$ .

Concerning the skeletal isomerization, promotion effect of  $H_2S$  appears for all three reactants. This can be reasonably explained by scheme (2). Namely,  $H_2S$  forms new acidic sites ( $H - Mo - SH$ ). This site may supply proton to adsorbed hydrocarbon species and carbonium ion so formed subsequently isomerizes. Present work seems to be concerned with the recently reported promotion effect of  $H_2S$  on HDN reaction,<sup>2,3)</sup> since both of ring saturation and subsequent hydrogenolysis are important steps for HDN reaction.<sup>7)</sup>

References 1) R.Ramachandran and F.E.Massoth, *J.Catal.*, **67**, 248(1981). 2) S.H.Yang and C.N.Satterfield, *Ind. Eng. Chem. Proc. Des. Dev.*, **23**, 20(1984). 3) A.S.Hirschon and R.M. Laine, *Fuel*, **64**, 868(1985). 4) H.C.Lee and J.B.Butt, *J.Catal.*, **49**, 320(1977). 5) D.H.Broderick, A.V.Sapre, B.C.Gates, H.Kwart, and G.C.A.Schuit, *J.Catal.*, **73**, 45(1982). 6) S.Gultekin, S.A.Ali, and C.N.Satterfield, *Ind. Eng. Chem. Proc. Des. Dev.*, **23**, 179(1984). 7) A.V.Sapre and B.C.Gates, *Ind. Eng. Chem. Proc. Des. Dev.*, **20**, 68(1981).

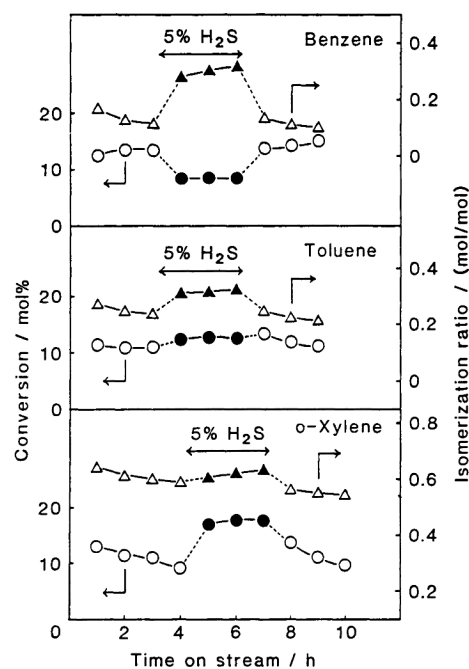


Fig.1. Effect of  $H_2S$  addition on conversion and isomerization.

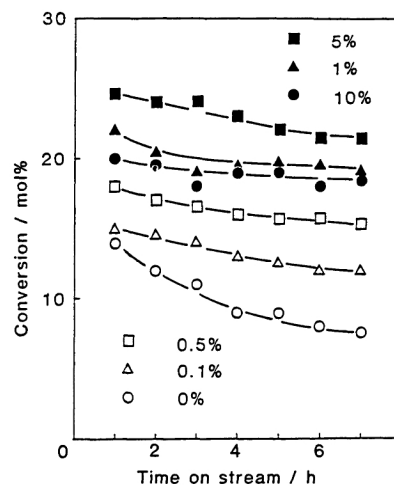


Fig.2. Effect of  $H_2S$  concentration on hydrogenation of *o*-xy.

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