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Effect of H_2S on Hydrogenation Activity of Sulfided $Co/Mo/Al_2O_3$

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Effect of gas-phase H_2S on the reactions of aromatic hydrocarbons over sulfided $Co/Mo/Al_2O_3$ was studied at 400 °C. The added H_2S inhibited hydrogenation of benzene but accelerated hydrogenation of o-xylene. No effect was exerted upon hydrogenation of toluene. At all instances, the added H_2S accelerated skeletal isomerization.

Presulfided $Co/Mo/Al_2O_3$ 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_2S with the feed. Reported results appear, however, to be quite conflicting. The gas-phase H_2S has been shown to promote hydrogenative reactions in a number of instances,1-3) but the contrary has also been reported frequently.4-6) We report, in the present paper, the effect of the gas-phase H_2S on the reactions of benzene, toluene, and o-xylene over a presulfided $Co/Mo/Al_2O_3$ catalyst. These compounds are chosen as probe substrate, since they are known to be not so reactive in hydrogenative reaction,7) and hence results are expected to reflect catalysts activity more clearly.

A conventional flow reactor was used. Three grams of a commercial $Co/Mo/Al_2O_3$ catalyst(4.4 wt% CoO and 14.9 wt% MoO_3) was placed in the reactor vessel. Prior to the test runs, the catalyst was presulfided with $H_2S(5\%)/H_2(95\%)$ gas mixture of 1 MPa at 400 °C. Reactions were carried out at 400 °C and 5 MPa with LHSV 4.5 h^{-1} and H_2/Feed of 1000 vol/vol. Product compositions were determined by a gas chromatograph equipped with a 50 m OV-101 glass capillary collumn.

The products observed were as follows; cyclohexane and methylcyclopentane for benzene, methylcyclohexane and dimethyl-, ethyl-cyclopentane for toluene, dimethylcyclohexanes 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_2S on hydrogenation activity was examined by adding H_2S to H_2 flow in stepwise so as to be 5% by volume. As is shown in Fig.1, the added H_2S 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_2S 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. $H_2S \longrightarrow 2Ha + S$ (1). Thus the main role of H_2S is to modify the catalyst surface as follows. $Mo + H_2S \rightleftharpoons H - Mo\text{-}SH \rightleftharpoons Mo\text{-}S + H_2$ (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,[2,3] since both of ring saturation and subsequent hydrogenolysis are important steps for HDN reaction.[7]

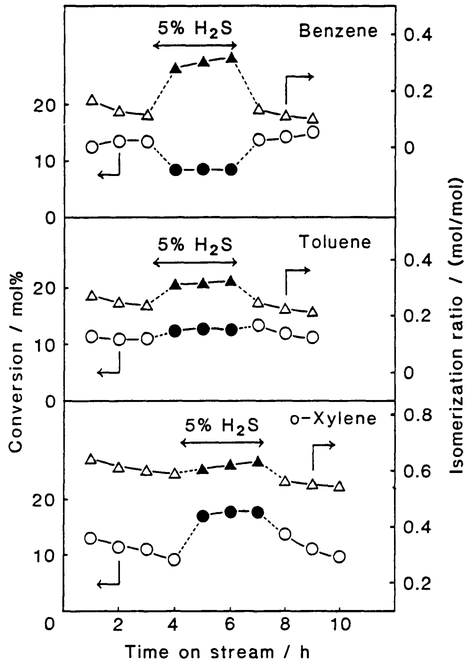

Fig.1. Effect of H_2S addition on conversion and isomerization.

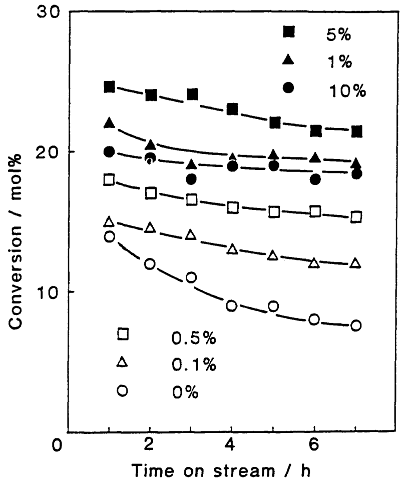

Fig.2. Effect of H_2S concentration on hydrogenation of o-xy.

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).

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