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NOTE

The Bifunctional Character of Hydrorefining Catalysts in Benzothiophene Hydrodesulphurization

The mechanism of hydrodesulphurization (HDS) of aromatic sulphur heterocycles is a subject of continuing discussion (*1–4*). We believe that independently of temperature, pressure, and catalyst, the necessary first step of HDS, preceding the cleavage of the C–S bond, is hydrogenation to destroy the aromaticity of the thiophenic ring (*4–6*). Such a course of HDS was suggested already in early studies (*7*) and is shown for the reaction of benzothiophene in Fig. 1 ("Other intermediates" in Fig. 1 are C–SH compounds and styrene). This concept has recently been further developed, e.g., by Kwart *et al.* for thiophene (*1*), Geneste *et al.* for benzothiophene (*8*), and Singhal *et al.* for dibenzothiophene (*2*). We have criticized (*4–6*) the concept of direct hydrogenolysis of the aromatic C–S bond which is illustrated, for example, by the mechanisms proposed by Lipsch and Schuit (*9*) or Okamoto *et al.* (*10*). We regard the equation of this direct hydrogenolysis, which is represented in Fig. 1 by the broken line, as a mere formal stoichiometric relation (*4–6*). It fits the formal kinetics based on bulk phase analysis (*3, 8, 11*), but it does not correspond to any real chemical process at the catalyst surface.

In this situation we may expect that studies of the behaviour of saturated cyclic sulphur intermediates in HDS should provide important experimental material to clarify the reaction mechanism and the role of the individual components of HDS catalysts.

The literature data uniformly indicate that the selectivity to saturated intermediates (tetrahydrothiophene (THT) or 1,2-dihydrobenzothiophene (DHBT)) in the consecutive scheme in Fig. 1 (simply designated as "selectivity" in the following text) is higher in the reaction of benzothiophene (BT) than in that of thiophene (T) and that it is higher at high hydrogen pressures and low temperatures. This variability does not indicate the change of the mechanism (*4–6*). However, the influence of catalyst composition has been studied to a very limited extent only. The lower selectivity has been observed for catalysts containing a polar alumina carrier rather than for catalysts with a nonpolar carrier (active carbon) or without carrier (*6*). Other papers dealing with saturated intermediates (*3, 8, 11, 12*) used always only one catalyst and do not provide any information about the influence of the individual components of the catalyst or details of its preparation. It is our intention to study these factors.

In the first step of these studies, we have compared the selectivity of the essentially random set of commercial and laboratory-prepared HDS catalysts. The purpose of this note is to report on the principal result that their selectivities differ considerably and to stress the importance of this observation. The results obtained hitherto do not allow detailed discussion of the relation between the catalyst composition and its selectivity and this is the reason why only basic information about catalysts is summarized here. Catalyst I (Mo/Al_2O_3) was prepared by impregnation of commercial Al_2O_3 carrier (Ketjen) by ammonium molybdate; II ($Ni–Mo/Al_2O_3$) was prepared by impregnation of I (Mo/Al_2O_3) by nickel nitrate; III ($Ni–Mo/Al_2O_3–SiO_2$) was a pi-

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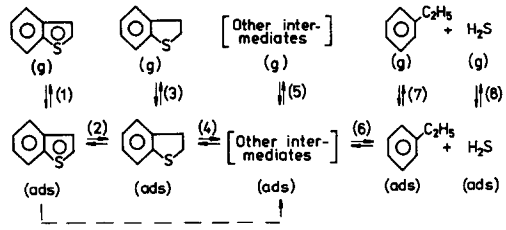

FIG. 1. The reaction sequence of HDS of benzothiophene. (g)—gas phase, (ads)—adsorbed.

lot plant sample (Chemické závody ČSSP, Czechoslovakia); IV (Ni–Mo/Al_2O_3) was a commercial catalyst Ketjenfine 153-1.5E (Ketjen); V (Co–Mo/Al_2O_3) was a commercial product Cherox 36-01 (Chemické závody ČSSP), and VI (Ni–W/Al_2O_3) was a commercial product Cherox 34-02 (Chemické závody ČSSP). Catalysts were crushed to 0.16–0.25 mm particle size fraction and were sulphided by a H_2S/H_2 (1 : 8) mixture at 673 K for 4 h, cooled in N_2, and stored in air atmosphere.

Benzothiophene was used as a model compound because the higher concentrations of DHBT formed by its reaction are more accurately measurable than smaller amounts of THT by the reaction of TH. The pressure tube flow reactor used was described elsewhere (*4*, *5*). The charge of sulphided catalyst was heated in H_2 flow to the temperature of the measurement. The solution of BT (Fluka) in *n*-decane (Reakhim) was next fed in such a way that the molar ratio of H_2, decane, and BT was 90 : 5 : 1, respectively. The reaction temperature was 543 K and the total pressure was 2.1 MPa. Each run at one space time lasted 1 h. The condensate was analysed by GLC as described elsewhere (*4*). The total conversion of BT, x(BT), and the conversion of BT to DHBT, x(DHBT), were calculated using the equations $x(\mathrm{BT}) = (n^0(\mathrm{BT}) - n(\mathrm{BT}))/n^0(\mathrm{BT})$ and $x(\mathrm{DHBT}) = n(\mathrm{DHBT})/n^0(\mathrm{BT})$, where $n^0(i)$ and $n(i)$ are the moles of component i in the feed and products, respectively. Both the activity and selectivity attained a steady state after an initial 20 min of feed and all conversions reported here are mean values observed during the next 40 min.

The conversions obtained are plotted in Fig. 2 in the coordinates x(DHBT) – x(BT). The kinetic function $x(\mathrm{DHBT}) = f(x(\mathrm{BT}))$ defines the selectivity of a catalyst and is a characteristic intensive property of it. All catalysts having the same quality of active surface must exhibit, under identical conditions, i.e., temperature and initial partial pressures of reactants, identical dependence $x(\mathrm{DHBT}) = f(x(\mathrm{BT}))$. This dependence was determined for catalyst V (Co–Mo/Al_2O_3) by nine points covering the whole region of $x(\mathrm{BT}) = 0–1.0$ (catalyst charges from 0.05 to 1.8 g and space times from 3.5 to 120 [g(cat) h (mol(BT))$^{-1}$]. For all other catalysts, the course of x(DHBT) $= f(x(\mathrm{BT}))$ was tested by the measurement of only two points with space times 7.3 and 12.8 (0.1-g catalyst charge). The broken lines in Fig. 2 represent the functions $x(\mathrm{DHBT}) = f(x(\mathrm{BT}))$ obtained by extrapolation using these two points for each catalyst. This extrapolation is only approximate, particularly in the region of the maxima of the curves. Nevertheless, Fig. 2

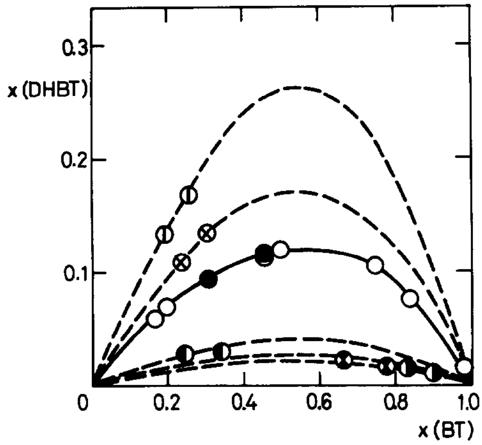

FIG. 2. The dependence of the conversion of benzothiophene to 1,2-dihydrobenzothiophene on the total conversion of benzothiophene at 543 K and 2.1 MPa. Catalyst charge, 0.1 g: (⦶) I (Mo/Al_2O_3); (⊗) II (Ni–Mo/Al_2O_3); (●) V (Co–Mo/Al_2O_3); (◕) III (Ni–Mo/Al_2O_3–SiO_2); (◑) IV (Ni–Mo/Al_2O_3); (◐) VI (Ni–W/Al_2O_3); other catalyst charges: (○) V (Co–Mo/Al_2O_3).

shows unambiguously that the catalysts differ considerably in selectivity, which is determined by the shape of $x(\mathrm{DHBT}) = f(x(\mathrm{BT}))$, and consequently, they have a different quality of active surface.

The different quality of active surface of the catalysts, proved by the results in Fig. 2, means that the active surface is not formed only by MoS_2 or WS_2. The carrier and promoter not only influence the stability and area of the surface of MoS_2 or WS_2 but they directly participate in the reaction sequence and so change the ratio of the rates of steps (1)–(4) in Fig. 1. Their effect is further dependent on the details of catalyst preparation. We suggest that the most promising hypothesis to plan further experiments and to explain these effects is to regard HDS catalysts as bifunctional catalysts. This concept was used originally to explain their hydroisomerization and hydrocracking activity (*7*). It assumes that two functions of the catalyst cooperate in these reactions, namely, a hydrogenation–dehydrogenation function and an acidic (cracking) function. No specific activity for hydrogenolysis of the C—C bond is assumed because this is considered to be assembled from the hydrogenation and the acidic functions (*7*). We have suggested that also HDS can be sufficiently explained in terms of only these two functions (*4–6*). It is assumed that aromatic sulphur rings are first hydrogenated (hydrogenation function), the saturated C—S bonds are then cracked (acidic function) with formation of unsaturated C=C bonds which are then hydrogenated (again hydrogenation function). It should be stressed once more that this interpretation does not assume the existence of the hydrogenolysis step and that it must be distinguished from other duality concepts of HDS catalysts, e.g., the "hydrogenation–hydrogenolysis" concept (*3, 11*) or the "weak acid sites for HDS and strong acid sites for hydrogenation" concept (*7*).

The saturated intermediate in Fig. 1 is formed by a hydrogenation reaction and is removed by the consecutive sequence of cracking and hydrogenation reactions. (This assumption sufficiently explains the pressure and temperature dependence of the selectivity (*4–6*).) So, the different selectivity of various HDS catalysts in Fig. 2 is considered to be the manifestation of the different ratio of hydrogenation and acidic functions of these catalysts. The detailed interpretation requires further systematic study. However, two points seen in Fig. 2 are worthy of mention. Firstly, comparison of catalysts I and II, which are related by preparation, shows that the addition of Ni to Mo/Al_2O_3 catalyst decreases the selectivity. We observed previously that addition of Co to Mo/carbon catalyst decreases the selectivity to THT in HDS of T. This suggests that promoter generally decreases the kinetic stability of saturated intermediate relative to aromatic reactant. Secondly, the data in Fig. 2 put forward the existence of a relation between the selectivity and total desulphurization activity, the latter being expressed as $x(\mathrm{S}) = n(\mathrm{H_2S})/n^0(\mathrm{BT})$ at constant space time. This activity can be read out for each catalyst from Fig. 2 using the relation $x(\mathrm{S}) = x(\mathrm{BT}) - x(\mathrm{DHBT})$. The values at space time 12.8 are for molybdenum-based catalysts I–V: 8, 17, 33, 76, and 89%, respectively. Comparison at space time 7.3 provides the same order. This order of activity is inversely proportional to the selectivity, which is determined by the course of $x(\mathrm{DHBT}) = f(x(\mathrm{BT}))$ in Fig. 2. Tungsten-based catalyst VI deviates from this correlation. The importance of both these facts is stressed by the fact that at medium hydrogen pressures, the problem seems to be not to hydrogenate BT, but to decompose DHBT (see, e.g., data at 8 MPa by Daly (*12*)).

The results confirm that studies of the behaviour of saturated intermediates in the HDS reaction provide material which can significantly contribute to a better understanding of the mechanism of the reaction and of the role of the individual components of HDS catalysts.

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