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NOTES

Hydroprocessing of Substituted Benzenes over a Sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ Catalyst

Previous papers (*1*, *2*) have reported that substituted benzenes are suitable model compounds for evaluating the hydrogenolysis vs ring hydrogenation activity of a conventional sulfided $NiMo/Al_2O_3$ hydrotreating catalyst. The two reaction paths for the hydroprocessing of substituted benzenes are illustrated in Fig. 1. We have shown, in particular, that ring hydrogenation is favored by strongly electron-donating substituents such as NH_2, NHC_6H_5, OH, or OC_6H_5, whereas hydrogenolysis is favored by slightly electron-donating substitutents such as SH, SC_6H_5, Cl, or Br. Moreover, the Hammett-type correlations obtained have confirmed the predominant influence of the aromatic character of organic molecules on the reactivity. The presence of such correlations constituted the first chemical evidence for the existence of two distinct catalytic sites, one responsible for the hydrogenation of the benzene ring, associated with an electron-withdrawing character, and the other responsible for the hydrogenolysis of the $C_{sp^2}\text{–}X$ bonds, associated with an electron-donating character.

The literature data concerning the hydroprocessing of substituted benzenes show that $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts behave differently. For example, the hydrodeoxygenation of methyl-substituted phenols proceeds mainly through hydrogenolysis of the C–O bond over a sulfided $CoMo/Al_2O_3$ catalyst (*3*) and the authors concerned have also proposed that different active sites were responsible for the two reaction paths (see Fig. 1), one for C–O bond cleavage and another for hydrogenation. Over a sulfided $NiMo/Al_2O_3$ catalyst, we have shown that the hydrodeoxygenation of phenols substituted by alkyl, cycloalkyl, or phenyl groups occurs mostly through ring hydrogenation (*4*). A similar difference in behavior between the two catalytic systems has also been observed for the hydrodeoxygenation of diphenylether, where the cleavage of the C–O bond is more important over a sulfided $CoMo/Al_2O_3$ (*5*) than over a sulfided $NiMo/Al_2O_3$ catalyst (*6*).

From a recent compilation of results obtained under similar operating conditions in our laboratory for numerous model compounds and those reported in the literature, we arrived at the conclusion that the difference between $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts lies in the hydrogenolysis rather than in the hydrogenation properties (*7*). It was thus interesting to consider the behavior of a $CoMo/Al_2O_3$ catalyst toward a series of X-substituted benzenes as was done with the $NiMo/Al_2O_3$ catalyst. This could provide further information concerning the interactions between the catalyst and the organic molecules, the nature of the catalytic sites, and the mechanism of hydrogenation and hydrogenolysis reactions.

Experiments were carried out in a 0.3-liter stirred autoclave, operating in a batch mode at 340°C and 70 bar of hydrogen pressure (see Refs. (*4*, *6*) for typical procedure). No H_2S or H_2S precursor was added to the feed. The $CoMo/Al_2O_3$ catalyst was Procatalyse HR 306 which has the following composition: 3% CoO, 14% MoO_3, and 83% $\gamma\text{-}Al_2O_3$. It was sulfided at atmospheric pressure using a fluidized-bed technique with a gas mixture of 15% H_2S and 85% H_2 by volume. The catalyst was heated in flowing H_2/H_2S (gas flow, 120 ml/min) from 20 to 400°C (8°C/min) and held at 400°C for 4 h, then cooled, and finally swept with nitro-

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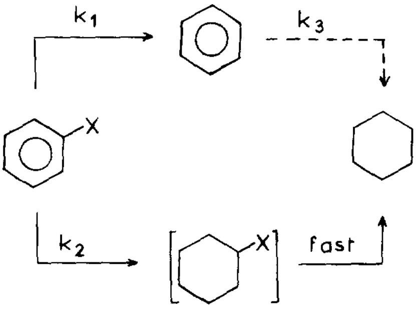

FIG. 1. Reaction network for hydroprocessing of *X*-substituted benzenes over sulfided catalysts (*X* = H, OH, OC_6H_5, SH, SC_6H_5, NH_2, NHC_6H_5, F, Cl, Br).

gen for 30 min. Analyses were performed on a Girdel 30 gas chromatograph equipped with a flame ionization detector using hydrogen as carrier gas, and capillary columns (Chrompack CP Sil 5 CB or CP Sil 19 CB, 25 m × 0.22 mm i.d.). Products were identified by comparison with authentic samples. The rate constants were deduced from the experimental plots of concentrations vs time by curve fitting and simulation, assuming all the reactions to be first order in the organic reactant.

The hydroprocessing of substituted benzenes over the $CoMo/Al_2O_3$ HR 306 catalyst proceeds through the reaction network given in Fig. 1. The disappearance rate constants and the percentages of benzene and cyclohexane formed are reported in Table 1. The percentages of hydrogenolysis of the C–*X* bonds are, as expected, higher over the $CoMo/Al_2O_3$ catalyst than over the $NiMo/Al_2O_3$ catalyst previously used. This agrees well with other results concerning HDO of phenols (*3*) and HDN of aniline (*8*) over $CoMo/Al_2O_3$ catalysts. The rate constants for the hydrogenolysis of the C–*X* bond (k_1) and those for the hydrogenation of the benzene ring (k_2) have been calculated from the relative concentrations in benzene and cyclohexane, respectively, as previously described (*1, 2*). These rate constants are reported in Table 2 together with those obtained over the $NiMo/Al_2O_3$ HR 346 catalyst in order to compare more easily the behavior of the two catalysts.

For the sulfided $CoMo/Al_2O_3$ HR 306 catalyst the hydrogenolysis activity is higher for slightly electron-donating substituents such as SC_6H_5, Cl, Br, or F, whereas the hydrogenation activity, in its turn, is maximum for strongly electron-donating substituents such as NH_2, OH, or OC_6H_5. One can thus expect to have correlations of the kind observed over the $NiMo/Al_2O_3$ HR 346 catalyst (*1, 2*). This is seen by plotting the logarithms of the rate constants of hydrogenation (Fig. 2) and hydrogenolysis (Fig. 3) as a function of the substituent parameter σ_R accounting for the electron-do-

TABLE 1

Rate Constants ($\times 10^3$ min^{-1}/g catalyst) for the Disappearance of *X*-Substituted Benzenes over the Sulfided $CoMo/Al_2O_3$ HR 306 Catalyst at 340°C, 70 bar H_2 and Percentages of Benzene and Cyclohexane Formed

Compounds	*k*	% benzene	% cyclohexane
Diphenylsulfide	126 (300)	100 (99)	Traces (=1)
Bromobenzene	60 (100)	100 (99)	Traces (=1)
Chlorobenzene	44 (75)	100 (99)	Traces (=1)
Fluorobenzene	45 (10)	100 (80)	Traces (20)
Diphenylether	37 (6)	68 (50)	32 (50)
Phenol	70 (35)	41 (5)	59 (95)
Aniline	25 (11)	81 (10)	19 (90)
Benzene	1 (2)	— (—)	100 (100)

Note. The corresponding data for the sulfided $NiMo/Al_2O_3$ HR 346 catalyst are given in brackets.

TABLE 2

Hydrogenolysis (k_1) and Hydrogenation (k_2) Rate Constants ($\times 10^3$ min^{-1}/g catalyst) over Sulfided CoMo HR 346 and NiMo HR 346 Catalysts at 340°C, 70 bar H_2

Compounds	k_1(CoMo)	k_1(NiMo)	k_2(CoMo)	k_2(NiMo)
Diphenylsulfide	126	300	~1[a]	2
Bromobenzene	60	100	~1[a]	2
Chorobenzene	44	75	~1[a]	2
Fluorobenzene	45	8	~1[a]	2
Diphenylether	25	3	12	3
Phenol	28	2	42	33
Aniline	20	1	5	10
Benzene	—	—	1	2

[a] This lower limit, given as the rate constant for hydrogenation of benzene, corresponds to ~1% of hydrogenation for diphenylsulfide and ~2% of hydrogenation for chloro-, bromo-, and fluorobenzene.

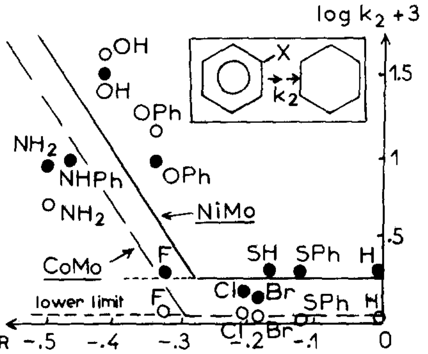

FIG. 2. Plot of the logarithms of the hydrogenation rate constants vs the resonance substituent constant σ_R over sulfided NiMo HR 346 (●) and CoMo HR 306 (O) catalysts at 340°C and 70 bar H_2.

nating ability of the substituents. Whatever the catalysts, the reactivity always depends on the aromatic properties of the organic molecules through π-electron delocalization.

For the hydrogenation of the benzene ring, the correlation is concerned only with the O-, N-, and F- substituents for kinetic reasons. Indeed, for Cl-, Br-, and S-substituted benzenes which undergo rapid formation of benzene through hydrogenolysis, the rate of hydrogenation of the benzene ring is limited by the hydrogenation rate of benzene itself (*1*, *2*). The slope values obtained by linear regression, −3.8 for the NiMo/Al_2O_3 catalyst and −4.1 for the CoMo/Al_2O_3 catalyst, are similar. This implies that the mechanisms of hydrogenation are the same for both catalysts. Although the number of data is limited and the data scatter is relatively important, such a similarity in the mechanisms of hydrogenation does not appear to be fortuitous. Numerous results show slight differences in the hydrogenation activity of sulfided CoMo/Al_2O_3, NiMo/Al_2O_3, NiW/Al_2O_3, and CoW/Al_2O_3 catalysts toward model compounds. This is the case not only for simple molecules such as substituted benzenes but also for heavier molecules such as dibenzothiophene, dibenzofuran, or carbazole (*9*). A similar value of the slope of the correlation would also indicate a similar sensitivity to the substituent effects. This value is of the same order of magnitude as the value found in electrophilic substitution reactions, in agreement with previous observations on the formation of a π-adsorbed complex in hydrogenation reactions (*2*, *3*) and on the existence of a similar active phase on the hydrogenation site of both catalysts, as already assumed (*2*, *10*).

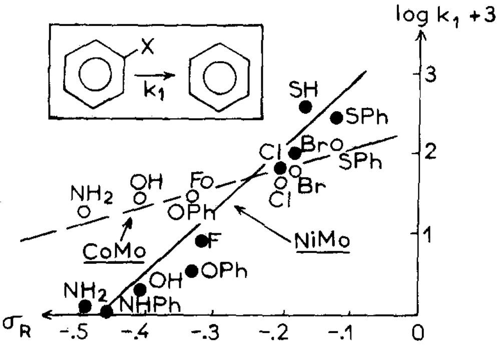

FIG. 3. Plot of the logarithms of the hydrogenolysis rate constants vs the resonance substituent constant σ_R over sulfided NiMo HR 346 (●) and CoMo HR 306 (O) catalysts at 340°C and 70 bar H_2.

For the hydrogenolysis of the C–*X* bond, the influence of the electron-donating ability of the substituents is less over the CoMo/Al_2O_3 catalyst (slope = +1.9) than over the NiMo/Al_2O_3 catalyst (slope = +7.5). The positive slope is indicative of an electron-donating character of the hydrogenolysis site, as already assumed (*1*, *2*). However, the lower slope value is indicative of a reduced participation of the substituents toward conjugation with the benzene ring through π-electron delocalization. This would mean a larger participation through σ-adsorption on the hydrogenolysis site of the CoMo/Al_2O_3 HR 306 catalyst as illustrated in Figs. 4a and 4b. As for the NiMo/Al_2O_3 HR 346 catalyst (*1*, *2*), the interactions between the organic molecules and the catalytic sites can be visualized in a similar manner, taking into account the signs of the slopes of the correlations obtained (Fig. 4a). Neverthe-

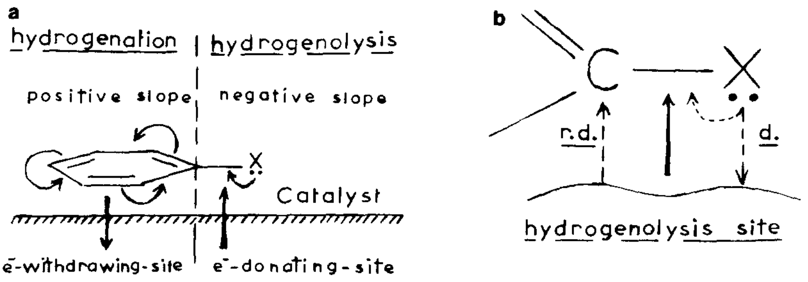

FIG. 4. (a) Dual-site mechanism for hydroprocessing of *X*-substituted benzenes over sulfided NiMo HR 346 and CoMo HR 306 catalysts at 340°C and 70 bar H_2. (b) Decomposition of total electron-donating ability of the hydrogenolysis site into donating effect of the substituent to the site *(d)* and retrodonating effect of the site to the C atom of the C–*X* bond (*rd*)

less, the effect observed for the hydrogenolysis reaction could result from a donating effect (*d*) of the substituent to the site of hydrogenolysis and a retrodonating effect (*rd*) of the site to the carbon atom of the C–*X* bond (Fig. 4b). This could also mean that the hydrogenolysis sites are more directly influenced by the promoter metal than hydrogenation sites (*2*). These new results can thus lead to further information on the mechanism of cleavage of C_{sp^2}–X bonds. Calculations are being considered which take into account both the properties of the molecules and the models of active sites.

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