JOURNAL OF CATALYSIS **83**, 245–247 (1983)

Hydroprocessing of Phenothiazine, Dibenzothiophene, and Thianthrene over Ni–Mo/Al_2O_3 Catalyst: Structural and Electronic Effects

In the course of our studies on the reactivity of benzothiophene (*1*) and sulfided polycyclic aromatic compounds (*2*) with respect to the hydrodesulfurization reaction (HDS), and following our studies of the influence of nitrogen-containing compounds on the HDS of benzothiophene, we have explored the reactivity of the phenothiazine molecule which contains the two hetero-atoms S and N. A recent work on the HDS reaction of this compound over CoMo-Al_2O_3 catalyst (*3*) has prompted us to report our first results.

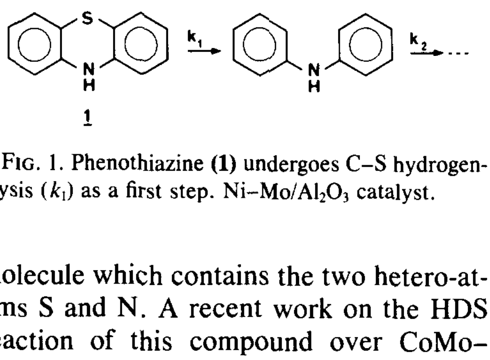

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FIG. 1. Phenothiazine (**1**) undergoes C–S hydrogenolysis (k_1) as a first step. Ni–Mo/Al_2O_3 catalyst.

The experiments were carried out in a 0.3 liter stirred autoclave (Autoclave Engineers type Magnedrive) operating in the batch mode, with a system for sampling of liquid during the course of the reaction. The catalyst was a Procatalyst HR 346 desulfurization catalyst (3 wt% NiO; 14 wt% MoO_3; 83 wt% Al_2O_3) which was presulfided, using a fluidized bed technique, in 3% H_2S in H_2 (*2*). Dodecane was used as carrier oil. Reaction products were analyzed by gas chromatography (Girdel 3000 using a flame ionization detector) with an OV 17 Pyrex column (separation conditions: injector, 300°C; detector, 300°C; temperature programming from 70 to 260°C at 7°C/min).

Analysis of the liquid samples from the phenothiazine reactions carried out under various conditions of temperature and H_2 pressure showed that in all cases hydrogenolysis of C–S bonds resulting in the formation of diphenylamine (Fig. 1) is the first step of the overall process. For lower temperatures and H_2 pressures (Table 1) diphenylamine did not react.

However, at higher temperatures and H_2 pressures (Table 1), the reaction can proceed further, involving hydrogenolysis of C–N bonds to give aniline and benzene before final hydrogenation to cyclohexane. In all cases, no organic sulfur-containing products were observed. When the hydroprocessing conditions of phenothiazine permit the reaction to be completed with the formation of cyclohexane, the product distribution versus time shows that the behavior of hydroprocessing of phenothiazine is that of a classical consecutive reaction network.

The rate constants of pseudo-first-order kinetics were determined from experimental results by curve fitting (and simulation)

TABLE 1

Rate Parameters Determined for Hydroprocessing of Phenothiazine Catalyzed by Ni–Mo/Al_2O_3

Reaction conditions	$k_1 \times 10^{3a}$ [$min^{-1} \cdot (g\ cat)^{-1}$]	$k_2 \times 10^{-3a}$ [$min^{-1} \cdot (g\ cat)^{-1}$]
250°C; 34 bar	4.2	—
250°C; 70 bar	6.1	—
300°C; 70 bar	20	5
340°C; 34 bar	32	3
340°C; 70 bar	50	14

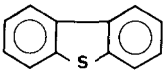
[a] Mean value of several runs.

0021-9517/83 $3.00

using a HP 9820 A computer equipped with a 9826 A tracing table.

Comparison of the rate constants for the first step corresponding to the C–S hydrogenolysis shows the effect of hydrogen pressure with a partial kinetic order of about $\frac{1}{2}$ in hydrogen. From the results obtained at different temperatures it was possible to determine an apparent activation energy of 63 kJ mol $^{-1}$ for the hydrogenolysis of the C–S bond.

In order to estimate the possible effect of the heteroatom N on the primary hydrodesulfurization reaction a direct comparison was made by Kwart *et al.* (*3*) between the rate of phenothiazine HDS and that of dibenzothiophene



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on Co–Mo/Al_2O_3. The agreement between the rate constants of these two molecules permitted the authors to suggest rather than a one-point adsorption reaction mechanism, a multipoint or ring adsorption on the catalyst surface in such a manner that the nitrogen atom could be involved (*3*).

However, the identical reactivity of dibenzothiophene and phenothiazine over Co–Mo/Al_2O_3 catalyst is rather surprising since (i) as pointed out by the authors themselves, nitrogen-containing species would adsorb strongly on active hydrodesulfurization catalytic sites and depress the rate of the HDS reaction (*3, 4*); (ii) as is well known from X-ray structure determination (*5, 6*) phenothiazine is folded along the S-N axis with a dihedral angle of 140°, while dibenzothiophene is planar (*7*).

In order to check these points we compared the reactivity of phenothiazine and dibenzothiophene on Ni–Mo/Al_2O_3 catalyst (Table 2). In these conditions the rate of desulfurization was seven times higher for phenothiazine than for dibenzothiophene. This result, in apparent contradiction with the expected inhibiting effect of the nitrogen atom, permits us to discuss the one-point adsorption mechanism vis-à-vis the flat multipoint or ring adsorption on the catalyst surface. The first one is considered to be implicated in the direct cleavage of the C–S bond by direct participation of hydrogen and the second one could imply a partial initial hydrogenation of the benzenoid ring to permit a β-elimination (*8*). The greater π-electron availability on the benzene ring of phenothiazine by virtue of the nitrogen atom, even partly reduced by the folding, most probably accounts for the higher rate, which is also amplified by the higher hydrogenating properties of the Ni–Mo catalyst (*9*).

TABLE 2

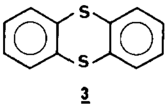
Rate Constants for Desulfurization of Phenothiazine and Dibenzothiophene, and Elimination of the First S-Atom in Thianthrene, Catalyzed by Ni–Mo/Al_2O_3 at 250°C and p_{H_2} = 40 bar

Compound	$k_1 \times 10^3$ [$min^{-1} \cdot (g\ cat)^{-1}$]
Thianthrene[a]	15
Phenothiazine	5
Dibenzothiophene[a]	0.7

[a] Ref. (*2*).

This result seems to be well in accordance with the multipoint adsorption mechanism since the HDS reaction is supposed to be related to the strength of adsorption and ease of hydrogenation of one of the aromatic rings.

In order to check the inhibiting influence of the nitrogen atom on the catalytic sites (*4*) the reactivity of phenothiazine was compared with that of the thianthrene molecule



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which is also folded along the S–S axis with a dihedral angle of 128° (*10*). The result illustrated the effect of the nitrogen atom on the desulfurization process since there was a lowering of the rate by a factor of 3 due to the difference in adsorption for N and S atoms.

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Received December 23, 1982

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