Catalytic Hydrogenolysis of Phenothiazine, Thianthrene, and Phenoxathiin

Masatoshi NAGAI* and Noriyuki SAKIKAWA

Department of Industrial Chemistry, Faculty of Science and Engineering, Nihon University,
Chiyoda-ku, Tokyo 101

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Catalytic hydrogenolysis of phenothiazine, thianthrene, and phenoxathiin as appropriate model reactants in the competing reactions of sulfur, nitrogen, and oxygen removal over NH_4Y zeolite, pre-sulfided Co–Mo–Al_2O_3, and Ni–W–$SiO_2Al_2O_3$ catalysts has been carried out using the batch method. The cleavage patterns and the schemes in the hydrogenolysis of the three compounds and the active sites of an NH_4Y zeolite for the hydrogenolysis are discussed. The C–S bond in phenoxathiin was more prone to cleavage than the C–O bond, and the C–N bond in phenothiazine was not broken in our experiments. Sulfur removal from the three compounds took place more than the removal of nitrogen or oxygen. The reactivity over the zeolite Y, pre-sulfided Co–Mo–Al_2O_3, and Ni–W–$SiO_2Al_2O_3$ catalysts decreased in the order of phenothiazine>phenoxathiin>thianthrene, but in the absence of the catalyst the thermal stability was phenoxathiin>thianthrene>phenothiazine. In the hydrogenolysis of the three compounds over the NH_4Y catalyst the desulfurization activity of the zeolite Y catalyst was maximized when calcined at 500 °C. The reaction of phenoxathiin was found to be accelerated by Brönsted acid, but this did not hold true in the case of phenothiazine and thianthrene.

In previous papers,[1,2] catalytic hydrodesulfurization of dibenzothiophene, one of the condensed thiophene compounds in residual oils, over an NH_4Y or CoY zeolite catalyst has been studied in order to elucidate the behavior of high-molecular-weight aromatic sulfur compounds.

Catalitic hydrodesulfurization of petroleum fractions or coal oils occurs concurrently with the removal of nitrogen and oxygen. Consequently, we carried out a model experiment on the competitive reactions of S, N, and O removal during the hydrogenolysis of fuel oils. Thianthrene, phenothiazine, and phenoxathiin containing two atoms of sulfur and nitrogen or oxygen atoms in the compounds are regarded as appropriate model reactants.

There have been many studies of the hydrogenolysis of sulfur, nitrogen or oxygen compounds alone.[3–6] However, the only studies of hydrogenolysis of thianthrene on a silica–alumina catalyst were reported by Tits-Skvortsova *et al.*[7] Badger *et al.*[8] studied the mechanism of the desulfurization reaction using Raney nickel. Aiken *et al.*[9] studied the behavior of cyclic sulfur compounds such as dibenzothiophene and thianthrene. There have been no studies of the reaction of phenoxathiin or phenothiazine.

In the present paper, the hydrogenolysis of thianthrene, phenothiazine, and phenoxathiin as the model compounds over NH_4Y zeolite, pre-sulfided Co–Mo–Al_2O_3, and Ni–W–$SiO_2Al_2O_3$ catalysts has been carried out in order to study the competitive reactions of desulfurization, denitrogenation, and deoxygenation. The mechanism of hydrogenolysis of the three compounds and the active sites of the NH_4Y zeolite are discussed.

Experimental

Reactants and Catalysts. Thianthrene was prepared by our modification of the procedure given by Shirley.[10] Phenothiazine and phenoxathiin were prepared by methods previously described;[11,12] thianthrene: mp 157—158.5 °C (lit,[10] 149—154 °C); phenothiazine: 186.5—187.5 °C (lit,[13a] 187 °C); phenoxathiin: 57—58.5 °C (lit,[12] 57.5—58 °C).

NH_4(61%)NaY zeolite was prepared from NaY by a conventional ion exchange procedure using a solution of NH_4Cl–NH_4OH. The exchanged zeolite was then washed thoroughly with decationized water and dried at 100 °C in air. The pretreatment of zeolite was as follows. Glass ampoules containing 0.65 g of zeolite were placed in a furnance. The temperature was slowly raised to the desired calcination temperature and maintained for 4 h, at which time equilibrium had been established, and then the ampoules were sealed. Co–Mo–Al_2O_3 and Ni–W–$SiO_2Al_2O_3$ catalysts obtained commercially were pre-sulfided with a H_2S/H_2 volume ratio of 1/5 at 350 °C for a period of 3 h in the autoclave.

Apparatus and Procedure. Hydrogenolysis of the three compounds was carried out in a 100 ml autoclave with a stirrer driven magnetically. The catalyst and the substrate (0.017 mol) were put into the autoclave, which was then charged with hydrogen to the required pressure. The autoclave was placed in an electric furnance and the temperature was slowly raised to 350 °C and was kept constant, hydrogenolysis being allowed to start after 2 h. After the reaction was completed the autoclave was cooled to room temperature and the liquid reaction mixture and hydrogen sulfide in the autoclave were collected for analysis.

Analytical. Analysis of the liquid reaction mixture was made by gas chromatography using a 3 m column filled with a 5% Silicone OV-17 supported on Chromosorb W. The column was maintained at 70 °C (in the case of the analysis of benzene, benzenethiol, and phenol), 80 °C (for aniline), or 200 °C (for other high boiling compounds). A helium carrier gas was used at the flow rate of 40 ml/min. Ethylbenzene (70, 80 °C) and acenaphthene (200 °C) were used as internal standards for the measurement of the weight of compounds. Hydrogen sulfide in the gaseous products was trapped by lead acetate solution, resulting in the formation of lead sulfide, which was determined by gravimetric analysis. Most of the components were identified through their characteristic retention times in the columns. However, diphenyl disulfide produced during thianthrene hydrogenolysis was isolated by gas chromatography, and was identified by comparing the retention time on gas chromatography, mp 58—60 °C (lit,[13b] 61 °C), IR spectrum, and the fragmentation of the mass spectrum with those of the authentic sample. The stability of the zeolite structure was checked by an X-ray

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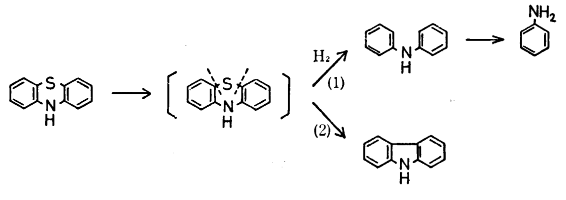
* Present address: Department of Chemical Engineering, Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184.

diffraction study. The degree of ion exchange was calculated from the sodium content of NH$_4$Y zeolite after ion exchange. Sodium was determined by chelate titration, using both uranyl acetate and nickel nitrate with a MX indicator.

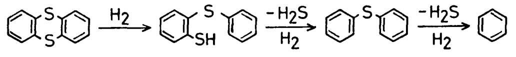
Results and Discussion

The Cleavage Patterns. *Phenothiazine*: Phenothiazine was desulfided in the highest compounds of thianthrene, phenoxathiin, and phenothiazine; the results for the hydrogenolysis of phenothiazine are given in Table 1. The data where the zeloite Y and no catalyst were used indicated that diphenylamine and a small amount of carbazole and aniline were observed in the products. Hence, the cleavage pattern and the pathways in phenothiazine hydrogenolysis over the NH$_4$Y catalyst were considered with Scheme 1. As diphenylamine was usualy produced in the presence of the pre-sulfided Co–Mo–Al$_2$O$_3$ and Ni–W–SiO$_2$Al$_2$O$_3$ catalysts, only pathway (1) appeared to be followed. Degradation reactions of diphenylamine and carbazole occur hardly at all, because benzene was not observed and very little aniline was produced. Because no dibenzothiophene was produced while carbazole was produced in the phenothiazine reaction, we concluded that the C–N bond in the molecule is not broken, while the C–S bond is easily broken.



Scheme 1.

Thianthrene: The results for the hydrogenolysis of thianthrene over the pre-sulfided Co–Mo–Al$_2$O$_3$, Ni–W–SiO$_2$Al$_2$O$_3$, and zeolite Y catalysts, and for the hydrogenolysis without catalysts are given in Table 2. Obolentsev and Mashkina[14] identified *o*-(phenylthio)-benzenethiol in thianthrene hydrogenolysis over a sulfided Co–Mo–Al$_2$O$_3$ catalyst and proposed Reaction Scheme 2. In our experiment, however, the products of thianthrene hydrogenolysis over the catalysts used were primarily benzene, diphenyl sulfide and diphenyl disulfide, and *o*-(phenylthio)benzenethiol could not be confirmed. Hence, Scheme 2 is doubtful.



Scheme 2.

It seems likely that the thianthrene molecule is distorted on the S–S line,[15] and that the molecule is adsorbed to the catalyst at one or usually at two sulfur atoms, while 2 or more of the 4 C–S bonds in the molecule

TABLE 1. CATALYTIC HYDROGENOLYSIS OF PHENOTHIAZINE*)

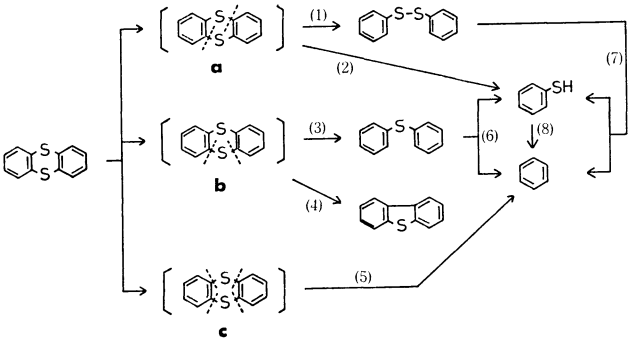
Catalyst	NH$_4$Y[a] 350 °C	NH$_4$Y[a] 500 °C	NH$_4$Y[a] 600 °C	None[b]	Ni-W-SiO$_2$Al$_2$O$_3$[c]	Co-Mo-Al$_2$O$_3$[d]
Sulfur removed[e] (mol%)	15.8	23.4	22.6	6.2	44.7	33.0
Percentage of products[f] (%)						
Benzene	0	0	0	0	0	0
Aniline	+	0.2	0.3	0	+	0
Diphenylamine	13.2	20.1	19.7	3.1	38.6	33.9
Carbazole	0.2	0.8	0.3	0.7	0	0
Phenothiazine	86.6	79.0	79.7	96.2	61.4	66.1

*) Hydrogenolysis conditions—catalyst, 0.65 g; initial hydrogen pressure, 50 kg/cm^2 (at 70 °C); reaction temp (a,b): 350 °C, (c,d): 250 °C. a) Zeolites prepared by calcination of NH$_4$Y at various temperatures. c,d) Pre-sulfiding condition—catalyst, 5 g; initial hydrogen pressure, 50 kg/cm^2 (room temp); time, 3 h. e) The yields were calculated from lead sulfide after the hydrogen sulfide in gaseous effluents was trapped in lead acetate solution. f) Products except gaseous effluents.

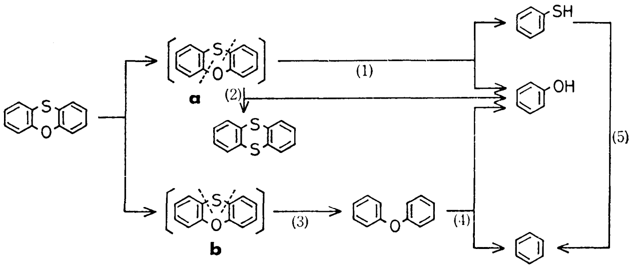
TABLE 2. CATALYTIC HYDROGENOLYSIS OF THIANTHRENE[a]

Catalyst	NH$_4$Y 350 °C	NH$_4$Y 500 °C	NH$_4$Y 600 °C	None	Ni-W-SiO$_2$Al$_2$O$_3$	Co-Mo-Al$_2$O$_3$
Sulfur removed (mol%)	9.1	13.4	12.5	1.3	7.2	15.0
Percentage of products (%)						
Benzene	3.5	19.7	23.7	0	0.8	11.8
Benzenethiol	1.2	2.1	0.8	0	0	0
I[b]	+	0.4	0.4	0	0	+
Diphenyl sulfide	1.7	3.5	4.0	0	3.4	5.9
Dibenzothiophene	1.0	3.3	2.8	2.2	0	0
Diphenyl disulfide	0.4	0.7	1.2	0	9.7	11.7
Thianthrene	92.0	70.4	67.1	97.8	86.2	70.6

a) The conditions in this table are similar to those in Table 1. b) Unidentified product.



Scheme 3.



Scheme 4.

are broken. We propose Scheme 3, which occurs with the three ways of cleavage (**a**, **b**, **c**), as a modification of Scheme 2 for thianthrene hydrogenolysis. When only an atom of sulfur is adsorbed and two C–S bonds are broken, and cleavage pattern (**b**) is expected to occur, pathways (3) and (4) are thought to take place. If it is assumed that thianthrene is adsorbed at both sulfur atoms, the hydrogenolysis of thianthrene proceeds according to cleavage patterns (**a**) and (**c**). In pattern (**a**), the two diagonal C–S bonds in thianthrene are simultaneously broken to give benzenethiol (2), or the S–S bonds form to give diphenyl disulfide, which is desorbed (1). On the other hand, in pattern (**c**) the simultaneous loss of two sulfur atoms from thianthrene results in the formation of benzene in pathway (5).

The amounts of the products given in Table 2 suggest that cleavage patterns (**a**) and (**c**) predominate in thianthrene hydrogenolysis over the pre-sulfided Co–Mo–Al_2O_3 and Ni–W–$SiO_2Al_2O_3$ catalysts. During pyrolysis, only pattern (**b**) occurred and the loss of an atom of sulfur allowed thianthrene to pass to the more stable planar form of dibenzothiophene (4).[16] In the presence of the zeolite Y catalyst, pattern (**b**) appeared to predominate over pattern (**a**).

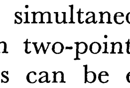
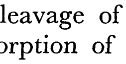
Phenoxathiin: The data for phenoxathiin hydrogenolysis over various catalysts are given in Table 3. The table shows that thianthrene and benzenethiol were produced in phenoxathiin hydrogenolysis over the NH_4Y zeolite catalyst, but were not observed over the pre-sulfided Co–Mo–Al_2O_3 and Ni–W–$SiO_2Al_2O_3$ catalysts and without catalysts. Grib *et al.*[17] reported that thianthrene and phenoxathiin were obtained by the reaction of diphenyl sulfide and diphenyl ether over an $AlCl_3$ catalyst, and that the formation of phenoxathiin was apparent, while that of thianthrene was not. We will now consider the hydrogenolysis mechanism (Scheme 4) which includes two kinds of cleavage patterns in order to explain the formation of thianthrene and benzenethiol and the absence of diphenyl sulfide in the products. For cleavage pattern (**a**) in Scheme 4 we assumed that the desorption of phenol is faster than that of benzenethiol, and that two molecules of benzenethiol combine on the surface of the catalyst to form thianthrene, which is then desorbed. Only in the case of the pre-sulfided Co–Mo–Al_2O_3 and Ni–W–$SiO_2Al_2O_3$ catalysts does cleavage pattern (**b**) take place.  and  are not thought to take place because diphenyl sulfide and dibenzothiophene were not observed in the products and because a little benzene was produced. The distribution of the products in Table 3 shows that the primary product was diphenyl ether produced by the fission of the C–S bond in phenoxathiin. The fact that cleavage of the C–S bond in one-point adsorption is easier than the simultaneous cleavage of the C–O and C–S bonds in two-point adsorption of the sulfur and oxygen atoms can be explained by the greater electron density of sulfur atoms compared with oxygen atoms.[18] When comparing the reactivity of the three compounds where no catalyst was used in Tables 1, 2 and 3, phenoxathiin is the most stable of the three compounds, and the thermal stability order is pheno-

TABLE 3. CATALYTIC HYDROGENOLYSIS OF PHENOXATHIIN[a)]

Catalyst	NH_4Y			None	Ni-W-$SiO_2Al_2O_3$	Co-Mo-Al_2O_3
	350 °C	500 °C	600 °C			
Sulfur removed (mol%)	8.9	13.4	6.6	1.0	34.1	26.8
Percentage of products (%)						
Benzene	2.5	5.1	3.5	0.3	0.6	0.7
Benzenethiol	1.2	0.4	+	0	0	0
Phenol	7.8	8.5	8.0	0	1.8	1.5
Diphenyl ether	5.7	15.1	11.6	0	31.6	19.0
Diphenyl sulfide	0.2	0	0	0	0	0
Phenoxathiin	81.7	67.6	75.4	99.7	65.9	78.9
Thianthrene	0.8	1.5	1.2	0	0	0
II[b)]	0	1.7	0.3	0	0	0

a) The conditions in this table are similar to those in Table 1. b) Unidentified product.

xathiin > thianthrene > phenothiazine. The reactivity of the compounds over the zeolite Y, pre-sulfided Co–Mo–Al_2O_3, and Ni–W–$SiO_2Al_2O_3$ catalysts, however, decreased in the order phenothiazine>phenoxathiin> thianthrene, which is different from the order in the absence of catalysts. The product percentages in Tables 1 and 2 show that diphenyl ether is less readily decomposed than diphenyl sulfide.

The Active Sites of NH_4Y Zeolite in the Hydrogenolysis. The percentage of sulfur removed (H_2S produced) in the hydrogenolysis of phenothiazine, thianthrene, and phenoxathiin over the NH_4Y zeolite catalyst as a function of the calcination temperature is shown in Fig. 1. The percentage of sulfur removed from all three substrates was greatest at a calcination temperature of *ca.* 500 °C, just as in the case of dibenzothiophene over the NH_4Y catalyst. The percentage of sulfur removed decreased in the order of phenothiazine>phenoxathiin>thianthrene. This order was the same when the Co–Mo–Al_2O_3 and Ni–W–$SiO_2Al_2O_3$ catalysts were used, as can be seen in Tables 1, 2, and 3. The activity of the zeolite catalyst during thianthrene reaction did not appreciably vary for calcination temperatures of the catalyst above 500 °C. The percentage of sulfur removed from phenoxathiin was greatly affected by the pretreatment temperature, reaching a maximum at 500 °C. The percentage of sulfur removed decreased sharply at temperatures above 500 °C. It has been proposed that the Brönsted acid sites on the NH_4Y zeolite are converted to Lewis acid sites when pretreatment is carried out at temperatures higher than 500 °C, as a result of the elimination of water.[19,20] Hence, the percentage of sulfur removed from phenoxathiin would be expected to decrease rapidly with decreasing Brönsted acid sites. The effect of the initial hydrogen pressure on the percentage of sulfur removed is given in Fig. 2. Sulfur removed during phenoxathiin hydrogenolysis increased considerably with increasing pressure of initial hydrogen. Therefore, the hydrogenolysis of phenoxathiin over the NH_4Y catalyst is accelerated by the Brönsted acid sites produced during calcination.

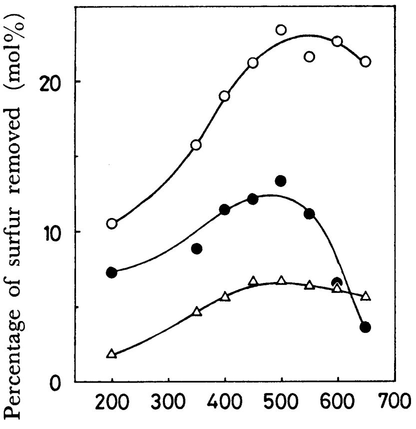


Fig. 1. The relations between the percentage of sulfur removed and calcination temperatures of the NH_4Y zeolite in the hydrogenolysis of phenothiazine (○), thianthrene (△), and phenoxathiin (●).

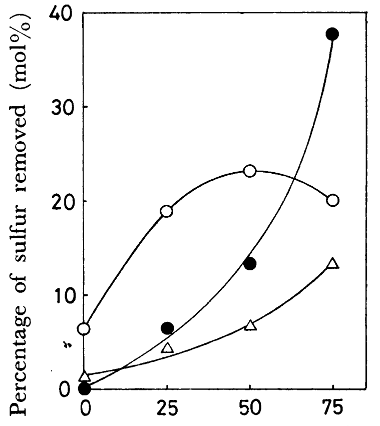
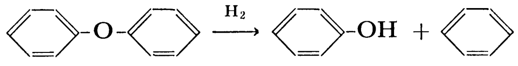


Fig. 2. The effect of the initial hydrogen pressure on the percentage of sulfur removed in the hydrogenolysis of phenothiazine (○), thianthrene (△), and phenoxathiin (●) over the NH_4Y catalyst calcined 500 °C.

More phenol than phenyl ether was formed in phenoxathiin hydrogenolysis over the NH_4Y catalyst calcined at 350 °C, but less phenol than phenyl ether was produced over the NH_4Y catalyst at calcination temperatures above 500 °C. This is thought to be due to the fact that the reaction:



is accelerated by the Brönsted acid sites produced at the lower calcination temperatures.

In the hydrogenolysis of phenothiazine and thianthrene it is not yet understood what acid sites promote the reaction. As in the hydrodesulfurization of dibenzothiopene, however, sulfur removal was greatest when zeolite prepared by calcination of NH_4Y at temperatures of *ca.* 500 °C was used. There can therefore be no doubt that the acid sites play a role in the hydrogenolysis reaction.

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