THE EFFECT OF SULPHUR COMPOUNDS ON HYDRODENITROGENATION OF NITROGEN COMPOUNDS ON A NICKEL–TUNGSTEN CATALYST

Mirko Černý

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Received July 16th, 1981

Hydrodenitrogenation of pyridine on a sulphided $NiO–WO_3/Al_2O_3$ catalyst has been studied in the presence of ethanethiol, propanethiol, thiophene and hydrogen sulphide and the amount of pentane, 1-methylpiperidine, 1-ethylpiperidine and piperidine has been determined. It was found that in the presence of all the sulphur compounds but hydrogen sulphide, the conversion of pyridine was lower than in their absence. The presence of hydrogen sulphide increased pyridine conversion.

Hydrodesulphuration (HDS) and hydrodenitrogenation (HDN) of naphtha fractions were studied on model compounds, mostly with single compounds and separately. In recent years it has been found that these two processes are closely related to each other and affect one another. The presence of pyridine and other basic nitrogen-containing heterocyclic compounds exerts negative effect on HDS of thiophene on industrial catalysts, where nitrogen compounds act as catalyst poisons. Similarly, also sulphur compounds affect HDN of nitrogen compounds. Thus, Satterfield found[1,2] that thiophene inhibits HDN of pyridine on sulphided Co–Mo, Ni–W and Ni–Mo catalysts at low or moderate temperatures. Only at temperatures above 350°C and a pressure of 7 MPa or above 390°C and a pressure of 1·14 MPa the addition of thiophene, although inhibiting the hydrogenation of pyridine to piperidine, increases the rate of cleavage of the piperidine formed. Under given reaction conditions this cleavage is determining factor. The result of these effects is the increase in the extent of hydrodenitrogenation. The effect of sulphur compounds on HDN of pyridine has been also studied by Weisser[3] who observed the positive effect of sulphur compounds on HDN of pyridine on sulphided Co–Mo and Ni–W catalysts in benzene solution for the whole temperature and pressure region studied (240–350°C, 7–8 MPa), and that both in an autoclave and in a flow reactor. The favourable effect of hydrogen sulphide on hydrocracking activity of Co–Mo catalysts has been reported also by Goudriaan[4] who carried out HDN of pyridine in xylene solution in the presence of thiophenol.

This work continues our previous studies which were concerned with the mechanism of cleavage of nitrogen compounds on sulphided Co–Mo, Ni–W and Ni–Mo catalysts[5–7]. Conclusions about mechanism have been based on detailed analysis of reaction mixtures. Piperidine ring undergoes hydrogenolytic cleavage to give pentylamine which reacts further to give a series of higher boiling heterocyclic compounds formed by transalkylation and cracking reactions. Final products of hydrogenolysis are ammonia and pentane. In order to make the identification of

eventual products easier, ethanethiol, propanethiol and thiophene were added in relative large amounts. We have also examined the effect of the above mentioned sulphur compounds on time dependence of formation of main products of hydrodenitrogenation reaction. The hydrogenolysis of pyridine on a sulphided Ni–W catalyst was made in the absence of solvents, which ensured the more reliable analysis of the reaction mixture. Hydrodenitrogenation of pyridine occurred at a temperature of 300 °C in an autoclave, initial hydrogen pressure being 6 MPa. After heating the autoclave to the reaction temperature, the hydrogen pressure increased to 11–12 MPa. At fixed time intervals the samples of the reaction mixture were taken and analysed by gas chromatography. By this method we determined the amount of pentane and pentene, 1-methylpiperidine, 1-ethylpiperidine, piperidine and pyridine. Besides pyridine, also mixtures of pyridine with ethanethiol, propanethiol, thiophene and hydrogen sulphide were subjected to hydrodenitrogenation. The composition of reaction mixtures is presented in Table I.

TABLE I

Composition of reaction mixtures in HDN of pyridine in the presence of sulphur compounds

Initial mixture	Time h	Pentane + pentene, %	1-Methyl-piperidine %	1-Ethyl-piperidine %	Piperidine %	Pyridine %
Pyridine	1	0·05	0·04	0·40	1·4	94·0
	3	0·12	0·09	0·89	2·9	88·9
	5	0·25	0·14	1·2	3·6	85·9
Pyridine + EtSH	1	[a]	[a]	0·30	1·2	82·9[b]
	3			0·47	1·8	81·4
	5			0·39	1·7	79·3
Pyridine + PrSH	1	[a]	[a]	0·39	1·5	83·7[c]
	3			0·50	2·1	83·0
	5			0·44	2·0	81·6
Pyridine + thiophene	1	[a]	[a]	[a]	[a]	80·7[d]
	3					79·1
	5					78·3
Pyridine + H_2S	1	0·14	0	0	1·2	90·4
	3	0·25	0	0	1·0	86·3
	5	0·66	0	0	0·7	80·0

[a] Not determined with sufficient accuracy. The initial mixture contained [b] 87·3% pyridine, [c] 84·8% pyridine, [d] 83·3% pyridine.

EXPERIMENTAL

Pyridine. The compound used was rectified pyridine of UV spectrograde purity.

Catalyst. Industrial Cherox-34-02 catalyst containing 3·5% NiO and 27% WO_3 on Al_2O_3 was ground and the fraction with 0·24—0·40 mm particle size was reduced in a stream of hydrogen at 450°C for 4 h and then it was sulphided by a mixture of hydrogen with hydrogen sulphide (9 : 1) at 400°C for 3 h. After decreasing the temperature to 100°C, the catalyst was allowed to cool in a stream of nitrogen.

Analysis of reaction mixture was made on a gas chromatograph equipped with a flame ionisation detector, using a column (3 m long) filled with 4% poly(ethylene glycol) 1 500 + 3% KOH on Chromosorb W.

Hydrogenation experiments were carried out in a 100 ml rocking autoclave which was heated electrically. The time at which the thermocouple placed in thermocouple well of the reactor indicated the temperature of 295°C was considered as the beginning of the reaction. This was achieved in approx. 120 min after the beginning of heating. The reaction temperature 300°C was kept with the accuracy of ±5°C. Samples for analysis were taken by means of two needle valves and their composition was determined with the use of standard mixtures of known composition. The samples were taken after 1 h, 3 and 5 h from the beginning of the reaction. The reaction was performed with 20 g of pyridine and 0·50 g of the catalyst. The sulphur compounds were added in the following amounts: ethanethiol 2·9 g (the pyridine to thiol molar ratio = 1 : 0·185), propanethiol 3·6 g (mol. ratio = 1 : 0·186), thiophene 4·0 g (mol. ratio = 1 : 0·188). Hydrogen sulphide was introduced in the following way. The autoclave was flushed with hydrogen, then hydrogen sulphide from pressure cylinder was introduced into the autoclave until the pressure reached 1·7 MPa and then the autoclave was pressurized by hydrogen to 6·0 MPa. The molar ratio of pyridine to hydrogen sulphide was 1 : 0·225. In the course of HDN of pyridine in the presence of hydrogen sulphide, both needle valves were clogged by solid reaction products after removal of two samples and the third sample (after 5 h) had to be taken from the autoclave after its cooling and opening.

RESULTS AND DISCUSSION

Formation of pentane and pentenes. In HDN of pyridine, the amount of both hydrocarbons increased monotonously with reaction time. In the presence of hydrogen sulphide, the amount of these hydrocarbons was twice as large, which documents the favourable effect of the sulphide in HDN of pyridine. In HDN of pyridine carried out in the presence of ethanethiol, propanethiol and thiophene, these sulphur compounds decompose to give substances which on chromatographic analysis overlap with C_5 hydrocarbons.

Formation of piperidine. In HDN of pyridine, the formation of piperidine had normal course. However, in the presence of hydrogen sulphide, the amount of piperidine in the reaction mixture decreased gradually. From experimental data it follows that during the first hour of hydrogenolysis, the amount of piperidine remains nearly constant. The gradual decrease in the amount of piperidine after this period is due to both the decreasing activity of the catalyst in pyridine hydrogenation and by the effect of hydrogen sulphide on the cleavage of piperidine ring. The effect of these

important factors is evident also in HDN of pyridine in the presence of ethanethiol and propanethiol, where only after three hours one observes the more distinct influence of the hydrogen sulphide formed from both thiols. As thiophene is the most stable of the above mentioned thiols and is cleaved to hydrogen sulphide at a slower rate, the hydrogen sulphide does not affect the course of the hydrogenolytic reaction during 5 h and thus it is not responsible for increased amount of piperidine, since at this period the decrease in piperidine formation by catalyst poisoning has not occured.

1-*Methylpiperidine.* It was found that the reaction mixture from HDN of pyridine carried out in the presence of hydrogen sulphide did not contain 1-methylpiperidine. This surprising fact is most likely caused by the substantially faster cleavage of 1-methylpiperidine compared to that of piperidine in the presence of hydrogen sulphide or rather by the different mechanism of the cleavage of piperidine ring in the presence of hydrogen sulphide. Products of decomposition of ethanethiol, propanethiol and thiophene made again the accurate determination of this compound impossible.

1-*Ethylpiperidine.* In contrast to HDN of pyridine itself, in which case the formation of 1-ethylpiperidine increases monotonously, in HDN of pyridine carried out in the presence of hydrogen sulphide, this compound is not formed in detectable amounts. In HDN of pyridine in the presence of ethanethiol and propanethiol, the negative effect of hydrogen sulphide begins to operate after 3 h of the reaction and the amount of 1-ethylpiperidine, passing through maximum, begins to decrease. This decrease or the absence of this compound in the reaction mixture obtained by HDN of pyridine in the presence of hydrogen sulphide are obviously due to the same reason as in the case of 1-methylpiperidine.

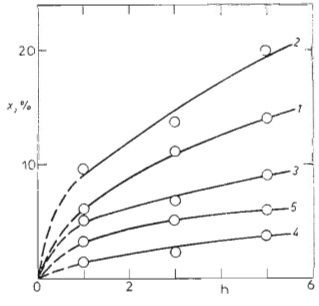

FIG. 1

Pyridine conversion in HDN of pyridine in the presence of sulphur compounds. *1* Pyridine, *2* pyridine + H_2S, *3* pyridine + + EtSH, *4* pyridine + thiophene, *5* pyridine + PrSH

Pyridine. In HDN of pyridine itself and of pyridine in the presence of hydrogen sulphide, *i.e.* in cases where the initial charge contained 100% of pyridine, the amount of pyridine in the reaction mixture decreases regularly in both cases. In the presence of hydrogen sulphide, the content of pyridine in the reaction mixture is by 5·9% lower after 5 h. Analytical data obtained had to be corrected, since in this case the reaction mixture contained also the products formed by interaction of piperidine or of its hydrogenolytic products with hydrogen sulphide. In other cases it was necessary to take into account that the initial mixture in HDN of pyridine in the presence of ethanethiol contained 87·3 per cent of pyridine, in HDN of pyridine in the presence of propanethiol it contained 84·8 per cent of pyridine and in the presence of thiophene it contained 83·3 per cent of pyridine.

The total conversion of pyridine in HDN of pyridine itself and in the presence of sulphur compounds is shown in Fig. 1. From this figure and data on the pyridine content presented in Table I it becomes evident that the conversion of pyridine in the presence of hydrogen sulphide is higher than is in the absence of the latter compound. These data are mutually well comparable, since in both cases the initial compound was pure pyridine. In contrast to it, the other curves for pyridine conversion in the presence of ethanethiol, propanethiol and thiophene are ladden with a certain error which is caused by the fact that these compounds decompose during the reaction and thus their content gradually decreases.

REFERENCES

1. Satterfield C. N., Modell M., Mayer J. F.: AIChE J. *21*, 1100 (1975).
2. Satterfield C. N., Modell M., Wilkens J. A.: Ind. Eng. Chem., Process Des. Develop. *19*, 154 (1980).
3. Weisser O., Dolanský J., Mostecký J.: Chem. Prům. *29/54*, 243 (1979).
4. Goudriaan F., Gierman H., Vlugter J. C.: J. Inst. Petrol. London *59*, 40 (1973).
5. Černý M.: This Journal *44*, 85 (1979).
6. Černý M.: This Journal *45*, 2215 (1980).
7. Černý M., Kraus M.: This Journal *46*, 1348 (1981).

Translated by J. Hetflejš.