HYDROGENOLYTIC CLEAVAGE OF PYRIDINE ON DIFFERENT COBALT-MOLYBDENUM AND NICKEL-TUNGSTEN CATALYSTS

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Received August 6th, 1980

Composition of the reaction products formed by hydrogenation of pyridine at 300°C and 15 MPa in the presence of 15 sulphided and unsulphided molybdenum and tungsten catalysts promoted by cobalt and by nickel, respectively, using alumina as the support in most cases, has been examined. It has been proved that the catalyst composition affects both its hydrogenation activity and the ratio of transalkylation to cracking (or hydrocracking) reactions. Relations between the catalyst composition and its activity and selectivity found for the reaction of pyridine differ from those reported for hydrogenolytic cleavage of thiophene, hydrogenation and isomerisation of cyclohexene.

Cleavage of nitrogen-containing heterocyclic compounds to hydrocarbons and ammonia is one of important single reactions in catalytic hydrorefining of petroleum fractions and is therefore the subject of extensive research[1-10]. In relation to the mechanims of these transformations, of the results obtained so far, the following two are especially important: *1)* The action of hydrogen in the presence of catalysts leads first to hydrogenation of aromatic compounds containing nitrogen in the ring and *2)* consecutive reactions of the so formed saturated heterocyclic compounds which involve the cleavage of C—N bonds produce a mixture consisting of up to several tens of nitrogen-containing organic substances, mostly amines, which only in further stages of the process yield ammonia. Most authors consider these consecutive reactions as hydrogenolysis; only exceptionally it is assumed that disproportionation, isomerisation and cracking of amines play a principal role. The latter assumption has been justified by a previous work of our laboratory[11] which proved that one of the products of hydrogenolysis of piperidine, N-(1-pentyl)piperidine, gives under conditions of hydrogenolytic cleavage besides other compounds also isomeric N-(2-pentyl)piperidine and N-(3-pentyl)piperidine.

The present work is concerned with the examination of the relative importance of hydrogenation and other functions of different catalysts used for hydrorefining petroleum fractions. For this purpose we used the determination of relative proportion of piperidine and N-alkylpiperidines in the products of the reaction of pyridine with hydrogen at 300°C and 15 MPa. We assumed that the formation of N-alkylpiperidines indicates disproportionation (transalkylation) ability of catalysts and that the amount of these substances having alkyl group with less than five carbon atoms in the chain is, at least to a certain extent, the measure of their cracking or hydrocracking activity. In addition to the above factors, we have also followed the content of pentenes and pentane. Overall conversions were low, in order that consecutive reactions would not affect the results.

We have first performed exploratory experiments with different catalysts under standard conditions (reaction time 1 h) and then compared a series of cobalt–molybdenum catalysts of different composition in the course of the reaction (the reaction time up to 5 h). These cobalt–molybdenum catalysts were already studied in our laboratory with respect to their activity for hydrogenation of cyclohexene[12], hydrodesulphurisation of thiophene[12] and isomerisation of cyclohexene[13], and further with respect to surface concentration of molybdenum[14] and relations between their activity and electron reflectance spectra[15].

EXPERIMENTAL

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

Catalysts V1—V7 were prepared earlier in our Laboratory[12] by impregnation of industrial alumina carrier with ammonium molybdate and cobaltous nitrate. After drying, the catalysts were reduced in a stream of hydrogen at 550°C for 5 h and then were sulphided in a stream of hydrogen and hydrogen sulphide (8 : 1) at 450°C for 3 h. The catalysts had the following initial composition: V1 Co : Mo mol. ratio = 1 : 5, molar ratio of both metals to Al_2O_3 = 0·15, *i.e.* 1·5% CoO and 14·8% MoO_3 (by weight); V2 1 : 5, 0·05, 0·58 w. % CoO, 5·5 w. % MoO_3; V3 1 : 5, 0·10, 1·1 w. % CoO, 10·4 w. % MoO_3; V4 1 : 2, 0·10, 2·2 w. % CoO, 8·4 w. % MoO_3; V5 1 : 1, 0·10, 3·3 w. % CoO, 6·4 w. % MoO_3; V6 0·1, 12·4 w. % MoO_3; V7 0·1, 6·9 w. % CoO. Catalysts were sieved and fractions containing particles below 0·2 mm were used in experiments.

Catalyst G35 (Girdler) contained 10·2 w. % MoO_3 and 1·8 w. % CoO, catalyst Cherox 36—01 (Chemické závody, Litvínov) 13 w. % MoO_3 and 3·5 w. % CoO, catalyst Cherox 34—02 3·5 w. % NiO and 27 w. % WO_3, catalyst 83—76 (Leuna-Werke, GDR) had a similar composition. Further catalysts tested were experimental ones: VUCHVU 712 containing 19·9 w. % WO_3, 4·7 w. % NiO, 15·6 w. % SiO_2, 0·06% Na_2O, the residue is Al_2O_3, and VUCHVU 528 containing 17·2 w. % MoO_3, 4·6 w. % NiO, 13·4 w. % SiO_2, 0·02 w %. Na_2O, the residue is Al_2O_3. All the catalysts mentioned were activated in the same way as catalysts V1—V7. MoS_2 and WS_2 were taken from laboratory stock.

Hydrogenation of pyridine was carried out in a rocking 100 ml autoclave. Pyridine purified by rectification (20 g) and a catalyst (1 g) were heated to 300°C under an initial hydrogen pressure of 7·5 MPa and the time at which the thermocouple placed in the well of the autoclave indicated a temperature of 295°C was considered as the beginning of the reaction. The reaction temperature 300°C was maintained with an accuracy of ±5°C. Samples for analysis were removed by needle valves. Their composition was determined gas chromatographically, based on calibration with standard mixtures. In addition to identified compounds, the reaction mixture contained also further substances, the amount of which increased with reaction time (in the case of the cleavage of pyridine on MoS_2 at 340°C, the reaction mixture contained 77% of these compounds[16]). Part of these substances formed chromatographic peaks, most of them, however, were present as an essentially nonvolatile residue. In some experiments also the amount of 1,5-dipiperidinopentane was roughly estimated; with catalyst V2 and after 1, 3 and 5 h, the mixture contained respectively 0·1, 0·3 and 0·5 w. % of this compound.

RESULTS AND DISCUSSION

N-Alkylpiperidines which, besides other compounds, are the product of the cleavage of pyridine on cobalt–molybdenum and nickel–tungsten catalysts are formed from the primary formed piperidine by its alkylation with hydrocarbon fragments or more likely from piperidine and other amines by transalkylation reactions. Among N-alkylpiperidines, those prevailing in our experiments were N-ethylpiperidine and N-(1-pentyl)piperidine (Table I). N-Ethylpiperidine (and other N-alkylpiperidines containing alkyls lower than C_4) is of interest since one has to assume for its formation not only the presence of active sites which are able to catalyse hydrogenation and transalkylation, but also the sites on which there proceeds the cleavage of C—C bond either by cracking or by hydrocracking.

This reasoning was used in comparing the catalysts of different composition (Table II). Experimental data were used to calculate two ratios characterizing the relative activity of the catalysts for reactions of different types. The 2 × mol of N-alkyl piperidines: (mol of piperidine + 2 × mol of N-alkylpiperidines) ratio (the ratio T/H) expresses the relative proportions of transalkylation and hydrogenation activities. The ratio of mol of N-1-pentylpiperidine to mol of N-ethylpiperidine (the ratio T/K) is an approximate measure of transalkylation and hydrocracking activities.

TABLE I

Content of N-Alkylpiperidines and C_5 Hydrocarbons in the Reaction Mixture After Hydrogenation of Pyridine on Sulphided Catalyst V6 at 300°C and 15 MPa for 4 h

Alkyl in N-alkylpiperidine	% (by weight)
Methyl	0·55
Ethyl	2·61
1-Propyl	0·75
1-Butyl	0·10
1-Pentyl	2·40
2-Pentyl	0·005
3-Pentyl	0·005
Cyclopentyl	0·28
Pentane + pentenes	0·40

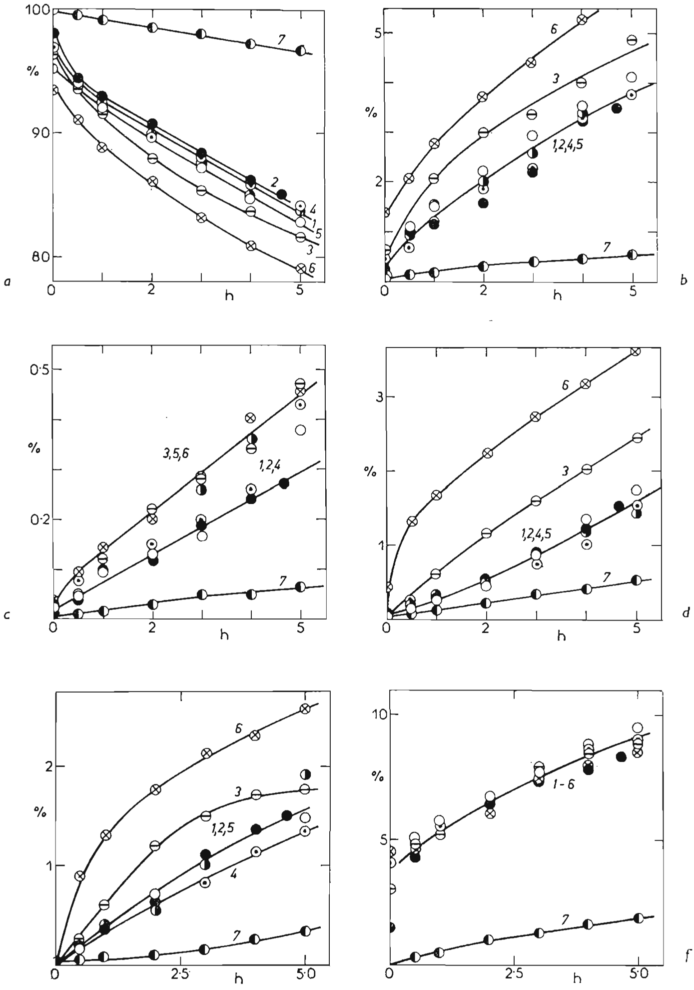
TABLE II

Main Reaction Products of Pyridine Hydrogenation on Different Catalysts

Temperature 300°C, hydrogen pressure 15 MPa, reaction time 1 h.

Catalyst	Piperidine, % w.	N-Methylpiperidine % w.	N-Ethylpiperidine % w.	N-1-Pentyl-piperidine, % w.	Pentane + pentene, % w.	T/K^a	T/H^b
V 4[c]	0·12	0·036	0·026	0·011	0·02	0·31	0·60
V 6[c]	0·25	0·021	0·031	0·010	0·03	0·24	0·37
V 4[d]	1·3	0·065	0·26	0·33	0·12	0·93	0·55
V 6[d]	3·2	0·33	1·40	1·54	0·16	0·93	0·71
Cherox 36-01[b]	12·0	0·17	0·77	1·20	0·25	1·14	0·30
Girdler G-35[b]	6·4	0·17	0·72	0·58	0·21	0·59	0·36
MoS_2	6·7	0·57	2·30	1·00	0·22	0·32	0·58
WS_2	4·1	0·31	1·20	0·54	0·21	0·33	0·55
Cherox 34-02[b]	6·2	0·28	0·61	0·73	0·35	0·87	0·36
Leuna 8376[b]	2·5	0·17	0·61	0·69	0·28	0·82	0·58
VUCHVU 712[b]	4·7	0·35	0·85	1·10	0·21	0·94	0·54
VUCHVU 528[b]	5·5	0·12	0·60	0·63	0·17	0·77	0·37

[a] T/K = mol of N-1-pentylpiperidine/mol of N-ethylpiperidine, [b] T/H = 2× mol of N-alkylpiperidines/(mol of piperidine + 2× mol of N-alkylpiperidines), [c] unsulphided, [d] sulphided.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From comparison of data presented in the first four rows of Table II it is evident that sulphidation affects the properties of cobalt–molybdenum catalysts significantly. In agreement with published data it is seen that sulphidation increases the activity of catalysts for hydrogenation of pyridine and exerts also pronounced effect of the T/K ratio. The T/H ratios do not indicate any systematic and significant differences between individual catalysts. By contrast to this, the sulphides, MoS_2 and WS_2, which were included into the series under study for purpose of comparison, differ markedly in this parameter ($T/K = 0{\cdot}32$ and $0{\cdot}33$, respectively) from sulphided supported catalysts. This indicates that the cracking activity can be ascribed mainly to the action of the carrier itself.

In further stage of this study we have been interested in differences in the course of the reaction of pyridine with hydrogen on catalysts V1 – V7. The amounts of main products are represented graphically in Figs $1a - 1f$. From inspection of the figure it becomes clear that the catalyst V7 not containing molybdenum differs from the other catalysts; the activity of cobalt is very low. The other catalysts differ only little from one another, the most active being apparently the catalyst V6 containing only molybdenum, and that not only as far as the position of the curves is concerned, but also with regard to the course of these curves in dependence on reaction time.

TABLE III

Comparison of Activity Sequence of Cobalt-Molybdenum Catalysts V1—V7 for Different Reactions

Reaction	Activity sequence
Hydrogenation of cyclohexene[12]	$3 > 1 > 2 \approx 6 > 4 > 5^a$
Hydrogenolysis of thiophene[12]	$3 > 4 > 5 > 1 > 2 > 6^a$
Isomerisation of cyclohexene	$1 > 2 \approx 4 \approx 6 > 3 \approx 5 > 7$
Hydrogenolysis of pyridine	$6 > 3 > 1 \approx 2 \approx 4 \approx 5 > 7$

[a] Catalyst V7 was inactive.

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FIG. 1

Main Components of Reaction Mixture Obtained by the Reaction of Pyridine with Hydrogen at 300°C and Maximum Hydrogen Pressure 15 MPa on Catalysts V1—V7 in Dependence on Reaction Time (in h)

Content of components is given in weight per cent, the designation of curves corresponds to that of catalysts V1—V7. Content of *a* pyridine, *b* piperidine, *c* pentane + pentene, *d* N-ethylpiperidine, *e* N-1-pentylpiperidine, *f* higher boiling substances.

This is important criterion since in our experimental arrangement the determination of the beginning of the reaction was uncertain. The autoclave had to be heated for one hour to attain the reaction temperature (295°C). The reaction proceeded also during this period, as demonstrated by conversions (even though low) at time $t = 0$. The catalyst V3 appears as second one in the activity sequence, the others cannot be distinguished from one another.

These findings are of interest in respect of the reported sequence of activities of these catalysts for hydrogenation of cyclohexene[12], hydrogenolytic cleavage of thiophene[12] and isomerisation of cyclohexene[13]. Qualitative comparison is presented in Table III; it follows that each reaction imposes different requirements on catalyst composition. This fact supports the recent conclusion of Katzer and Sivasubramanian[17] that industrial hydrorefining catalysts have been optimized with respect to their hydrodesulphurization activity and not with respect to dehydrodenitrogenation.

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Translated by J. Hetflejš.