STUDIES IN THE FIELD OF THE CATALYTIC SYNTHESIS OF PIPERAZINE

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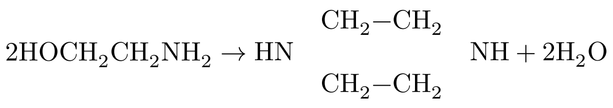
STUDIES IN THE FIELD OF THE CATALYTIC SYNTHESIS OF PIPERAZINE

Of great interest for the theory and practice of catalysis are works connected with the catalytic synthesis of heterocycles of the piperazine series, as well as of piperazine itself. Amino alcohols ($^{1-3}$), glycols (^{4}), and diamines (^{5}) may be used here as starting substances. The presence of several functional groups in the molecule determines the increased reactivity of these compounds and makes them a particularly convenient object in the study of such central questions of catalysis as the stagewise character and sequence of reactions and the selectivity of catalyst action. At the same time, piperazine and its homologues are substances possessing very diverse physiological effects. On their basis a whole series of effective medicinal preparations are produced. Piperazine, in particular, is known as a powerful anthelmintic. It may be widely used in the production of plastics, resins, rubbers, dyes, and pharmaceutical preparations.

The aim of the present study was the development of a catalytic synthesis of piperazine that could serve as the basis for a continuous process for obtaining piperazine from monoethanolamine. In the literature there are numerous data on the synthesis of piperazine from monoethanolamine (MEA). The reaction, as a rule, is carried out at high temperature and pressure in liquid ammonia in the presence of skeletal nickel (^{1,2}) or a nickel-copper-chromium catalyst (^{3}). The maximum yield of piperazine is 40–50%.

The reaction for obtaining piperazine from MEA



$$2HOCH_2CH_2NH_2 \rightarrow HN\begin{matrix}CH_2-CH_2\\ \\ CH_2-CH_2\end{matrix}NH + 2H_2O$$

is an intermolecular cyclodehydration reaction. However, as our experiments showed, dehydration catalysts such as activated Al_2O_3, trisubstituted calcium, iron, aluminum, and zinc phosphates, monosubstituted magnesium phosphate, phosphomolybdic acid, and others proved to be of low selectivity. The process was directed mainly toward the formation of ethylenimine and the products of its transformation.

On the other hand, it is known that in the amination reaction hydro-dehydrogenation catalysts such as nickel, copper, iron, and others are effective. Studies carried out by us on a series of different catalysts—metals—led to the conclusion that nickel and cobalt are the most active, whereas copper, iron, platinum, palladium, rhenium, and others practically do not cause cycloamination of MEA ([6]). It turned out that the support plays a substantial role and should rather be regarded as a component of a bifunctional catalyst. As supports we studied pumice, kieselguhr, silica gel, aluminosilicates, Al_2O_3 of various genesis, ZrO_2, TiO_2, ZnO, MgO, and Ca_3PO_4. The best of those studied proved to be a catalyst consisting of cobalt deposited on

γ-Al_2O_3 in an amount of 20 wt.% (Tables 1 and 2). A Ni—Al alloy proved to be fairly active (during the reaction it is leached), not inferior in activity to catalysts obtained by partial or complete leaching of the alloy. Nickel and cobalt obtained by decomposition from nitrate salts, carbonates, and oxalates are practically inactive in the process under study. Additives of various oxides (K_2O, ZnO, La_2O_3, Nd_2O_3, Bi_2O_3, MnO, ZrO_2, and TiO_2) and metals (Re, Pd) led, as

Table 1

Investigation of various catalysts in the reaction for obtaining piperazine from monoethanolamine
(initial hydrogen pressure 90 atm, MEA : NH_3 = 1 : 2.5 in moles)

Catalyst	Temp., °C	Pressure, atm	Time to attain max. piperazine yield, h	MEA, wt.%	piperazine, wt.%	ethylenediamine, wt.%	Piperazine yield based on reacted MEA, %
Ni—Al alloy	200	280	14	—	29.5	—	47.0
Ni—Al alloy, partially leached	200	290	36	—	31.3	10.2	44.5
Ni—kaolin	250	260	18.5	9.7	30.8	—	54.5
Ni—Al_2O_3—SiO_2	250	315	27	—	32.8	9.7	50.0

Catalyst	Temp., °C	Pressure, atm	Time to attain max. piperazine yield, h	MEA, wt.%	piperazine, wt.%	ethylenediamine, wt.%	Piperazine yield based on reacted MEA, %
Ni—γ-Al_2O_3	200	250	47	12.7	24.4	21.5	39.8
Ni—SiO_2	205	230	25	18.0	23.8	3.4	47.0
Co—γ-Al_2O_3	200	250	3	–	39.8	9.1	56.4
Co—kieselguhr	200	270	5	2.3	30.2*	6.8	42.8
Co—pumice	280	220	55	9.8	13.9	3.4	19.7
Co—ZrO_2	200	200	3	–	26.4	–	37.5
Co—Al_2O_3—SiO_2	200	260	14	17.8	20.5	13.1	24.8
Co—MgO	220	290	20	7.8	22.2	10.0	31.5
Co—ZnO **	200	290	14	40.5	7.8	6.6	18.6
Co—TiO_2	230	270	35	–	37.3	5.3	53.0
Co—α-Al_2O_3	235	280	50	2.2	21.1	4.9	30.0
Co—MgO—α-Al_2O_3	200	260	22	–	35.1	8.2	49.8
Effect of temperature							

Catalyst	Temp., °C	Pressure, atm	Time to attain max. piperazine yield, h	MEA, wt.%	piperazine, wt.%	ethylenediamine, wt.%	Piperazine yield based on reacted MEA, %
Co–Al_2O_3	170	210	15	–	30.0	–	42.5
Co–Al_2O_3	200	260	10	–	40.0	–	57.0
Co–Al_2O_3	222	205	4	–	33.0	–	47.0
Co–Al_2O_3(A-1)	200	250	6	–	38.6	9.3	54.8
Co–Al_2O_3(A-1)	220	270	4	–	32.0	8.3	45.5
Co–γ-Al_2O_3	170	240	36	–	41.7	7.2	59.4
Co–γ-Al_2O_3	200	250	3	–	39.8	9.1	56.4
Co–MnO–Al_2O_3	170	230	31	–	36.1	6.3	51.1
(MnO 0.5%)	200	260	5	–	37.9	5.0	53.9
(MnO 0.5%)	235***	270	3	–	36.2	6.2	51.4
(MnO 0.5%)	250***	260	1	–	19.7	5.1	28.0

* With a further increase in reaction duration, the piperazine concentration decreases.
** The catalyst was obtained by decomposition of oxalates; Co content—50%.
*** Further increase in reaction duration leads to a sharp decrease in the piperazine content.

a rule, to a decrease in the activity of Co—γ-Al_2O_3 and in the piperazine yield. Additives of MgO and BaO in amounts on the order of 0.5% cause a slight increase in the reaction rate and in the yield of the target product. The promoting effect of MgO is more clearly manifested in the case of the Co—α-Al_2O_3 catalyst (Table 1).

Study of the reaction conditions led to the conclusion that the optimum conditions are: temperature 200°, amount of catalyst (Co—γ-Al_2O_3) 10-15% of the weight of MEA, amount of ammonia 2.5-3 moles per 1 mole of MEA, initial hydrogen pressure 90-120 atm, and the pressure developed at the reaction temperature 220-270 atm. Under these conditions, in 3-6 h a piperazine yield of 55-60% of the theoretically possible is attained.

From the reaction mixture, in addition to piperazine, ethylenediamine, diethylenetriamine, N-(β-aminoethyl)-piperazine, and N-β-(-oxyethyl)-piperazine were isolated and identified by gas-liquid chromatography and IR and NMR spectroscopy. Figure 1 shows the accumulation curves for piperazine and other reaction products. It is seen from Fig. 1 that the concentration

piperazine continues to increase even after MEA has disappeared from the reaction mixture. In some cases, when the duration of the experiment is increased, the concentration of piperazine in the catalyzate decreases. Therefore, in comparing different catalysts, we did not confine ourselves to any one reaction time, but compared the product-accumulation curves at least up to the moment when the highest concentration of piperazine was reached. The accumulation curves for ethylenediamine and diethylenetriamine pass through a maximum, which indicates that they are intermediate products in the formation of piperazine.

It should be noted that ammonia and hydrogen play a role in this process. In the absence of NH_3 the process proceeds in another direction: mainly products of hydrogenolysis are formed, and only traces of piperazine. The presence of NH_3 is necessary throughout the entire experiment. Hydrogen, like NH_3, is a necessary component of the reaction, although formally they do not take direct part in it. Elucidation of the role of ammonia and hydrogen, as well as of the mechanism of this reaction, is the subject of our further investigations.

Fig. 1. Accumulation curves for the products of catalytic conversion of monoethanolamine (Co—Al_2O_3, 5780 Å, 220°, pressure 265 atm). 1 —water; 2 —piperazine; 3 —N-(β-aminoethyl)-piperazine; 4 —ethylenediamine; 5 —N-(β-hydroxyethyl)-piperazine; 6 —diethylenetriamine.

Experimental Part

Procedure for carrying out the experiments

The experiments were carried out in a rotating autoclave. During the experiment samples were withdrawn and analyzed. Quantitative analysis was performed by gas-liquid chromatography on a steel column (6 m) packed with polyethylene glycol (1%) deposited on NaCl containing 0.5% KOH (7). The yield of piperazine determined chromatographically is close to the yield of piperazine obtained as a result of distillation of the catalyzate.

Catalysts

Activated Al_2O_3 was impregnated with a solution of cobalt (nickel) nitrate, dried with stirring on a water bath, then in the catalytic tube in an air stream the nitrate salt was decomposed with a gradual rise in temperature to 450°; the catalyst was reduced in a stream of hydrogen, raising the temperature to 450° over the course of

Table 2

Effect of the ratio of monoethanolamine and ammonia
Catalyst Co—Al_2O_3, temperature 200°, initial hydrogen pressure —90 atm.

Amount of NH_3, mol per 1 mol MEA	Pressure at 200°, atm	Time to reach max. piperazine yield, h	Piperazine content in catalyzate, wt. %	Morpholine content in catalyzate, wt. %	Ethylenediamine content in catalyzate, wt. %	Piperazine yield based on reacted MEA, %
No ammonia	154	6	traces	MEA reacted completely	MEA reacted completely	—
0.6	220	4	24.8	—	4.0	35.2
1.3	240	3	22.8	5.4	2.8	32.3
2.5	270	10	40.0	—	1.5	57.0
4.2	280	5	28.8	9.4	2.4	35.2
6.0*	250	7	25.7	8.7	2.3	50.6
6.2	280	13	36.4	—	—	51.6

* Initial hydrogen pressure 60 atm.

bath, then in the catalytic tube in an air stream the nitric acid salt was decomposed with a gradual rise in temperature to 450°; the catalyst was reduced in a stream of hydrogen, raising the temperature to 450° during

6 h; at 450° the reduction was continued for 15-20 h. Other supported catalysts were prepared analogously. Skeletal catalysts were prepared by leaching a Ni—Al alloy (granules 2-4 mm in size) with 20% NaOH. Leaching was carried out both completely and partially (until the evolution of an amount of hydrogen corresponding to dissolution of half the aluminum). Table 1 gives test data for several catalysts.

Selection of optimal conditions. As is evident from the data in Table 1, with increasing temperature not only does the rate of conversion of MEA to piperazine increase, but also the rate of decomposition of piperazine. The optimal temperature is 200°, and this holds for several catalysts. Table 2 gives data on the effect of the MEA : NH_3 ratio on the reaction rate and the yield of the target product. The optimal ratio is 1 : 2.5. The total pressure also has a substantial effect on the course of the reaction. At a temperature of 200°, a molar ratio MEA : NH_3 = 1 : 2.5, an initial hydrogen pressure of 1 atm, and a total pressure at 200° equal to 140 atm, the yield of piperazine after 19 h was only 15.9%. The maximum yield of 55–60% is obtained at a pressure of 210–270 atm.

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Note: Figure translations are in progress. See original paper for figures.

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