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Pt/Al_2O_3 CATALYSTS IN THE SYNTHESIS OF NITROGEN HETEROCYCLES. CATALYTIC SYNTHESIS OF PYRAZINES

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A study was carried out on the use of Pt/Al_2O_3 catalysts in the synthesis of pyrazines via the dehydrogenation of piperazines, dehydrodeamination of diamines, and dehydrocyclocondensation of N-hydroxyalkyldiamines. In contrast to the current hypothesis of the intermediate formation of piperazine in the latter two reactions, evidence was found that these reactions proceed through initial dehydrogenation and the dehydrogenated intermediate then undergoes cyclization. Polyalkylpyrazines, formed by the alkylation of the pyrazine ring by hydrogenolysis products, are the major side-products in all the reactions studied. Pyrazines may be obtained in high yield and satisfactory selectivity by selecting suitable modifiers, which enhance the dehydrogenation activity of the catalyst and suppress the hydrogenolysis of the C—N bond.

Pyrazine and its homologs are used in the production of pharmaceuticals possessing anti-tuberculosis, antidepressant, antidiuretic, and antidiabetic activity as well as in the synthesis of insecticides, fluorescent dyes, and flavor additives for the food industry [1, 2]. Heterogeneous catalytic methods have been reported for the preparation of pyrazine and alkylpyrazines. The simplest of these methods involves the dehydrogenation of piperazines [3-8]. Other processes have been described, which use more available raw materials such as the dehydrodeamination of diamines [9, 10], dehydrocondensation of diamines with diols [11-13], olefin oxides [14-16], and formaldehyde [17], as well as the dehydrocondensation of aminoalcohols [18, 19]. The intermediate formation of the piperazine ring, which subsequently undergoes dehydrogenation, has been proposed in these multi-step processes:

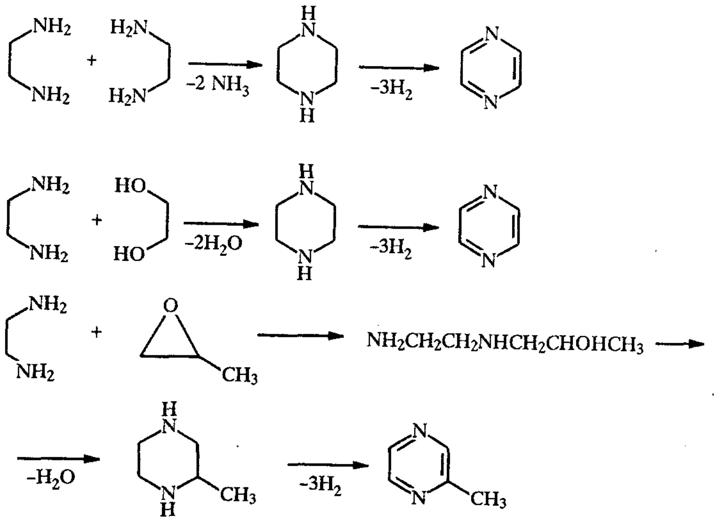

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TABLE 1. Conversion of Piperazine on Pt/Al_2O_3 Catalysts at 400°C (the volumetric piperazine inlet rate was 0.35 h^{-1}, the H_2:piperazine mole ratio was 7:1, and the reaction time was 4 h)

Experiment No.	Catalyst	Catalyzate yield, mass %	Content in catalyzate, mass %				Pyrazine yield mass %
			decomposition products	pyrazine	methyl-, ethyl- and dimethyl-pyrazine	pyrrole	
1	Pt (0,6%) — Al_2O_3 (catalyst)	68,2	4,0	63,0	33,0	Traces	43,0
2	Pt (0,6%) — Al_2O_3 — In_2O_3 (2,3%) (catalyst 2)	82,3	2,2	82,5	12,6	2,7	68,9
3	AP-56—In_2O_3 (2,3%) (catalyst 3)	84,1	1,3	84,2	12,1	2,4	71,2
4	(0,6%) — Al_2O_3 — In_2O_3 (2,3%) — Re_2O_7(0,5%) (catalyst 4)	84,3	0,8	92,9	5,6	0,7	78,7

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*The content of the active components are given in mass % here and in subsequent tables except for indicated cases.

Since each of these reactions involves dehydration (or deamination) and dehydrogenation, they may be carried out only in the presence of bifunctional catalysts. Pt/Al_2O_3 catalysts, which combine pronounced dehydrogenation capacity and acid activity and are commonly used in different processes for the conversion of hydrocarbons (gasoline reforming and the aromatization and dehydrogenation of paraffins), are typical bifunctional catalysts [20-22]. These catalysts have been studied extensively and methods have been developed to control their activity and selectivity, which facilitates their use in new reactions and industrial processes. It was therefore of interest to exploit the experience of the modifying Pt/Al_2O_3 systems for use in hydrocarbon conversions and check these systems in the synthesis of pyrazines by acting on some function of the catalyst. The dehydrogenation of piperazine on Pt/Al_2O_3 catalysts was studied in detail in our laboratory relative to the proposed participation of this compound as an intermediate in the abovementioned conversions [8]. The pyrazine yield does not exceed 43% on a bifunctional Pt/Al_2O_3 catalyst upon complete piperazine conversion (Table 1, sample 1). Most of the piperazine is consumed in side-reactions with the formation of coke, decomposition products, and alkylation products (25%). The latter are probably obtained as a result of the alkylation of pyrazine by decomposition products. After the addition of In_2O_3, which enhances the dehydrogenation function of the catalyst with a simultaneous diminution of its acid properties [23, 24], to the Pt/Al_2O_3 catalyst, the pyrazine yield rises to 70% (Table 1, samples 2 and 3). On the other hand, the amount of side-products remained rather high (up to 14%).

Pyrrole, which may be seen as the product of partial deamination of piperazine, was also formed in addition to alkylpyrazines. Stabilization of the dehydrogenation function of the catalyst by the introduction of Re_2O_7 facilitated a further increase in selectivity and the pyrazine yield rose to 80%, largely due to a decrease in the formation of alkylpyrazines and pyrrole. These results are not inferior to the best reported patent and literature data [3-7]. We should note that a good effect is also achieved by modification of waste AP-56 reforming catalyst (sample 3).

Dehydrodeamination of Ethylenediamine. The transformations of ethylenediamine on alumina, including systems containing dehydrogenating oxides such as MoO_3, WO_3 and CuO, have been extensively studied by Anderson et al. [9, 25, 26]. Linear deamination products such as triethylenediamine, cyclodeamination products such as piperazine, and, to a slight extent, dehydroaminocyclization products such as pyrazine are formed on alumina. An enhancement of the acid properties of the catalyst increases its deamination activity [26], while the introduction of components facilitating dehydrogenation leads to the formation of pyrazine. For example, pyrazine was obtained in 42% yield from ethylenediamine on an alumina catalyst containing 0.6% P_2O_5, 15% MoO_3, and 0.5% CuO. Haftendorn et al. [10] have described the preparation of pyrazine from ethylenediamine in the presence of a bifunctional catalyst containing 0.7% Pd on an alumosilicate support, whose acid function was somewhat reduced by the addition of CaO. The pyrazine yield was 75% [10].

TABLE 2. Pyrazine Formation from Ethylenediamine at 400°C (the volumetric rate was 0.6-0.7 h^{-1}, the H_2:ethylenediamine mole ratio was 1:1)

Experiment No.	Catalyst	Reaction time, h	Catalyzate yield, mass %	Product content in the catalyzate, mass %				pyrazine yield, %
				decomposition product	pyrazine	methyl-, ethyl-, and dimethylpyrazines	condensation products	
5	AP-64 (catalyst 5)	0...2	57,1	4,7	44,3	21,9	29,1	38,0
6-1	AP-64 к—In_2O_3 (2,4%)— Re_2O_7 (0,5%) (catalyst 4)	0...2	57,9	1,6	71,2	4,6	22,6	62,0
		2...4	57,4	1,0	68,8	3,6	26,7	59,4
6-4	Same	0...2	62,5	4,1	57,0	10,0	28,9	53,4
		2...4	62,1	3,5	61,0	8,2	27,3	56,8
6-5	Same	0...3	55,0	3,1	62,8	10,9	23,2	52,0
		3...5	57,5	2,9	65,8	8,9	22,4	57,0
		5...8	57,7	2,4	60,6	8,2	28,8	52,4
		8...10	56,0	1,7	65,4	8,2	24,7	54,8
7	NiO (5%)—Al_2O_3 (catalyst 10)	0...2	54,6	4,7	56,7	10,8	27,7	46,5
8	NiO (5%) — SiO_2 (catalyst 11)	0...2	38,5	6,3	27,1	38,3	28,8	15,8

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*After three similar runs with catalyst regeneration after each run.

The reaction mixture obtained in our work upon passing ethylenediamine through AP-64 bifunctional Pt/Al_2O_3 catalyst (Table 2, catalyst 5) is similar in composition to the mixture obtained upon the dehydrogenation of piperazine. The latter mixture contains 44.5% pyrazine, which corresponds to a 38% yield of this product. Methyl- and dimethylpyrazines as well as polyalkylpyrazines and other condensed products are formed in significant amounts. The addition of In_2O_3 and Re_2O_7 to AP-64 leads to an increase in the pyrazine yield (to 60%) due to a decrease in the yields of methyl- and dimethylpyrazines, though not to the same extent as in the dehydrogenation of piperazine. It is significant that this catalyst, which is inferior to the palladium/alumosilicate catalyst relative to pyrazine yields, proved rather stable upon prolonged use. The data given show that the pyrazine yields remained on a level close to the initial level upon multiple repetition of runs with the intermediate regeneration of pyrazine during a 10-h reaction cycle (compare runs 6-1 and 6-4, 6-5). Thus, an increase in the dehydrogenation function of the Pt/Al_2O_3 catalyst permits a significant increase in the pyrazine yield not only in the dehydrogenation of pyrazine but also in the dehydrodeamination of ethylenediamine.

Dehydrocondensation of ethylenediamine with propylene oxide has been described as a means for the preparation of methylpyrazine in a number of Japanese patents [14-16]. The product yields are much higher if N-(β-hydroxypropyl)ethylenediamine, which is readily formed upon mixing the starting reagents, is initially prepared. In the presence of dehydrating catalysts such as Al_2O_3 and phosphates, N-(β-hydroxypropyl)ethylenediamine forms methylpiperazine [27-29], apparently through intramolecular amination of the aminoalcohol with replacement of the hydroxyl group by an amino group [30]. If a bifunctional catalyst is used, intermediate methylpiperazine should be dehydrogenated to the corresponding pyrazine, as proposed by Shimanskaya et al. [25].

Table 3 gives the results of experiments on the conversion of N-(β-hydroxypropyl)ethylenediamine in the presence of Pt/Al_2O_3 and a few other bifunctional alumina catalysts. The methylpyrazine yield on AP-64 bifunctional Pt/Al_2O_3 catalyst (catalyst 5) was 22% at 350°C. There was a relatively small amount of dimethyl- and ethylpyrazines in the catalyzate but a large amount of condensed products. The introduction of In_2O_3 and Re_2O_7 (catalyst 4) increased the methylpyrazine yield to 43-45%. However, the amount of heavy components in the catalyzate was 30-35%, which is much greater than in the previous two cases.

The composition of the reaction products was studied in detail using GC/MS. The data in Table 4 show that a whole set of polyalkylpyrazines from dimethyl- to dimethylpropylpyrazine, is formed in addition to methylpyrazine. These products are probably formed by alkylation of the pyrazine ring by products of the decomposition of the starting N-(β-hydroxypropyl)ethylenediamine. Some alkylpyrazines undergo further transformations. For example, the formation of propenylpyrazines may be attributed to dehydrogenation of the propyl side-chain, while the formation of 5-methyl-6,7-dihydro-5H-cyclopentanepyrazine may be attributed to the subsequent condensation of the side-chain.

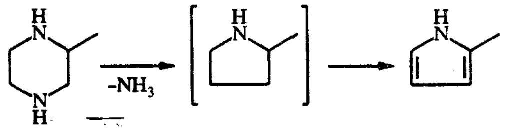
TABLE 3. Formation of Methylpyrazine from N-(β-Hydroxypropyl)ethylenediamine at 350°C (the volumetric inlet rate of the aminoalcohol was 0.66 h^{-1}, the H_2:aminoalcohol mole ratio was 1.3:1)

Experiment No.	Catalyst	Duration of experiment, h	Catalyzate yield, mass %	Content in catalyzate, mass %					methylpyrazine yield, mole %
				decomposition products	pyrazine	melts pyrazine	ethyl and dimethylpyrazines	condensation products	
9	AP-64k (catalyst 5)	0...1	64,8	8,7	6,1	26,4	6,2	52,6	22,0
10	Pt(0,6%)—Al_2O_3—In_2O_3 (2,4%) (catalyst 4)	0...2	87,6	12,3	3,5	44,0	5,4	34,8	43,0
		2...4	87,8	14,7	3,1	46,5	5,7	30,0	45,0
11	Pt(0,6%)—Al_2O_3—In_2O_3 (2,4%)—CuO(5%) (catalyst 6)	0...2	87,5	4,8	3,5	79,4	3,6	8,7	72,0
		3...4	86,3	5,1	3,2	69,7	7,8	14,2	62,1
12	ZnO—Al_2O_3(1 : 1, mole) (catalyst 7)	0...1	90,4	8,1	0,2	18,2	8,4	65,3	17,2
		0...1*	90,1	7,5	0,4	39,9	12,3	39,9	37,6
13	ZnO—Al_2O_3(9 : 1, mole) (catalyst 8)	0...1	92,1	3,0	3,7	32,1	16,1	45,1	31,0
		0...1*	90,3	5,5	1,0	61,2	8,7	23,7	57,6
14	CuO(5%)—ZnO—Al_2O_3 (ZnO—Al_2O_3, 9 : 1, mole) (catalyst 9)	0...1	88,5	2,2	0,4	86,5	8,0	2,9	79,4
		1...3	90,0	4,0	0,8	73,4	7,8	14,0	68,8
		3...4	90,6	4,4	1,0	62,1	7,0	25,5	58,8

TABLE 4. Composition of the Products of the Conversion of N-(β-Hydroxypropyl)ethylenediamine in the Presence of Pt/Al_2O_3 Catalyst at 350°C (the volumetric inlet rate was 0.66 h^{-1}, the H_2:aminoalcohol mole ratio was 1.3:1)

Mixture components	mass %	Mixture components	mass, %
1- and 2-Propanamine, 1- and 2-propanol, propanenitrile, 2-butanone, 3-pentanone	2,5	2-Methyl-6-propenyl- and 2-methyl-3-propenylpyrazines	0,9
Pyrazine	2,1	5-Methyl-6,7-dihydro-5H-cyclopentanepyrazine	0,4
Methylpyrazine	60,2	2-Methyl-, 3-methyl-, 2,5-dimethyl-, 2,3-dimethyl, 3-ethyl, 4-ethyl-2-methylpyrroles	2,1
2,5- and 2,6-Dimethylpyrazines	8,3	2-Methyl-, 2-ethyl-, 2,4-dimethyl-, 4-methyl-, 2-ethyl-4-methylimidazoles	3,1
Ethylpyrazine and 2,3-dimethylpyrazine	4,8	Not identified	1,5
2-Ethyl-6-methyl-, 2-ethyl-5-methyl-, and propylpyrazines	6,0		
2-Ethyl-3-methylpyrazine	4,1		
3-Ethyl-2,5-dimethyl, 2-ethyl-3,5-dimethyl-, 2,5-diethyl-, 2-methyl-5-propyl-, 2,3-diethyl-6-methyl-1,5-dimethyl-3-propyl-, 2,6-dimethyl-3-propylpyrazines	4,0		

Alkylpyrroles and alkylimidazoles were detected in addition to the pyrazine products. The formation of alkylpyrroles may be attributed to partial deamination of methylpyrazine with formation of a five-membered nitrogen ring, which is dehydrogenated to methylpyrrole and may be alkylated similar to methylpyrazine:



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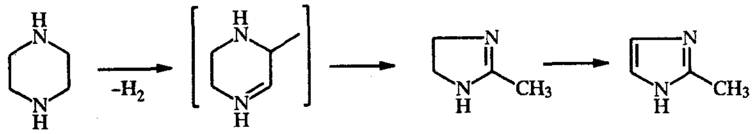
Alkylimidazoles may be obtained as the result of skeletal isomerization of the piperazine ring as considered in our previous work [8] on the dehydrogenation of piperazine in the presence of a $Pt/Al_2O_3—In_2O_3$ catalyst:



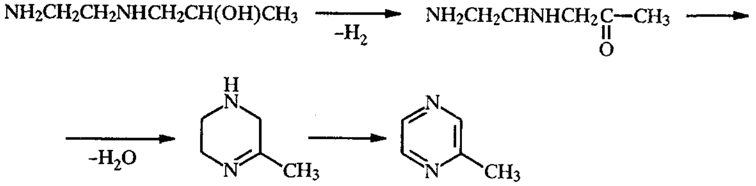
(5)

The same decomposition products apparently undergo other transformations leading to low-molecular-weight ketones, amines, and nitriles in addition to participating in alkylation (Table 4).

Polyalkylpyrazines comprise the major products, while minor amounts of many different side-products are formed. The introduction of copper into a nickel catalyst or gold into a platinum catalyst suppresses hydrogenolytic activity in hydrocarbon transformations and has a lesser effect on the dehydrogenation properties. We might expect that the addition of copper would suppress hydrogenolysis of the starting reagent or intermediate in the synthesis of methylpyrazine, thereby raising the selectivity for the major process. Table 3 shows that the introduction of 5% copper (catalyst 6) increases the reaction selectivity such that the methylpyrazine yield rises to 60-70% and the yield of the high-boiling products is reduced by a factor of 2.5-3.

The literature data on the efficiency of $ZnO—Al_2O_3$ systems in analogous reactions [11] suggested study of the transformations of N-(β-hydroxypropyl)ethylenediamine in the presence of a $ZnO—Al_2O_3$ catalyst with Al_2O_3:ZnO mole ratio equal to 1:1 and 1:9 (catalysts 7 and 8). The methylpyrazine yields on these catalysts at 350°C are much lower than on the Pt/Al_2O_3 samples and these yields could be raised to 37 and 57%, respectively, only at 400°C. As in the previous case, the addition of 5% copper led to an increase in the initial methylpyrazine yield to 80% though it then rapidly dropped and was only 59% at the end of a 4-h run.

The smoother formation of pyrazine and methylpyrazine on catalysts with suppressed acid properties and enhanced dehydrogenation function was rather unexpected in light of present concepts [25, 33]. These reactions presumably do not require the participation of acid sites and proceed only through dehydrogenation. For example, N-(β-hydroxypropyl)ethylenediamine may initially be dehydrogenated to give an aminoketone, which then cyclizes with the loss of water and formation of a cyclic Schiff base, namely, methyltetrahydropyrazine:

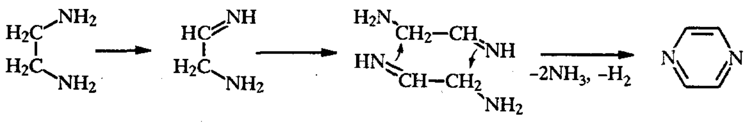


$$NH_2CH_2CH_2NHCH_2CH(OH)CH_3 \xrightarrow[-H_2]{} NH_2CH_2CHNHCH_2\underset{\underset{O}{\|}}{C}—CH_3 \longrightarrow$$

(6)

We should note that dehydrogenation of the alcohol group is one of the reaction steps. Thus, the pyrazine yield is rather high on catalysts containing ZnO and Cu, which are known to be active in the dehydrogenation of alcohols. The combined action of these components is especially successful. Hence, we may also understand the efficiency of zinc—chromium and copper—chromium systems proposed in a number of patents for the synthesis of pyrazines from N-(β-hydroxyalkyl) ethylenediamines [14-16]. The scheme proposed above also presupposes a different interpretation of the role of methylpiperazine, which is always found in greater or lesser amounts in the reaction mixture. In this case, methylpiperazine should be considered in this case not as an intermediate but rather as a reaction side-product formed, for example, as a result of the hydrogenation of methyltetrahydropyrazine.

An analogous dehydrogenation mechanism has been proposed for piperazine formation upon the dehydrodeamination of ethylenediamine. Imines or diimines may be formed as the primary products, which are capable of cyclodimerization with the elimination of two ammonia molecules:



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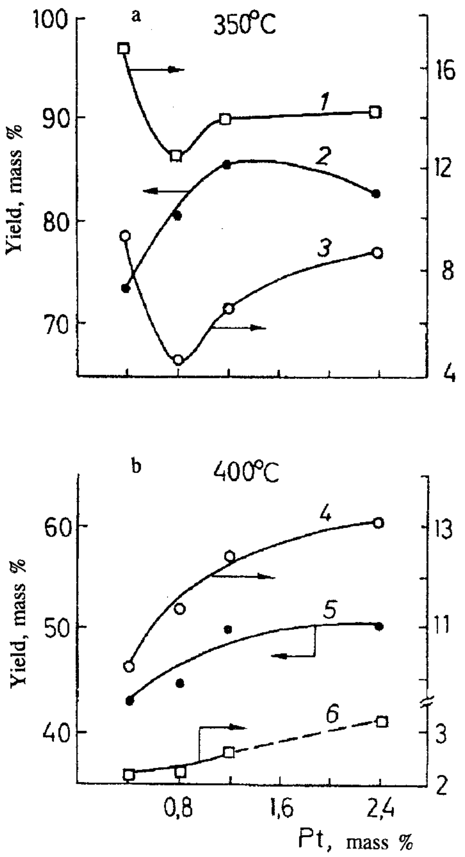

Fig. 1. Transformations accompanying the formation of methylpyrazine from $H_2NCH_2CH_2NHCH_2CHOHCH_3$ and of pyrazine from piperazine on the $Pt/Al_2O_3—In_2O_3$ catalyst: a) dehydrocondensation of $H_2NCH_2CH_2NHCH_2CHOHCH_3$ at 350°C, b) dehydrogenation of piperazine at 400°C: 1) polyalkylpyrazines; 2) methylpyrazine; 3) ethyl- and dimethylpyrazines; 4) methyl-, ethyl-, and dimethylpyrazines; 5) pyrazine; 6) pyrrole.

Kingsley et al. [34] has noted the possibility of a stepwise dehydrogenation of ethylenediamine on platinum atoms of the (1.1.1) face. The formation of pyrazine bases from diimines in the presence of a $Cr/K_2O-Al_2O_3$ catalyst has been described by Kondrat'eva and Dol'skaya [35].

Under actual reaction conditions, hydrogenolysis with subsequent alkylation of the pyrazine ring by the decomposition products occurs along with dehydrogenation. Hydrogenolysis usually accompanies dehydrogenation on metal or metal oxide catalysts [36]. Since both reactions proceed on metal sites, an increase in the metal surface in the catalyst, in principle, should be accompanied not only by an increase in the dehydrogenation activity of the catalyst but also an increase in hydrogenolysis. The hydrogenolysis of hydrocarbons proceeds only to a slight extent, in any case at about 400°C. Thus, an increase in the metal surface in the catalyst facilitates an increase in the yields of the dehydrogenation products. In the case of nitrogen compounds, we would expect an increase in hydrogenolysis processes in light of the lower strength of the C—N bond in comparison with the C—C bond. In this case, the yield of the dehydrogenation products may decrease with increasing metal surface due to competing hydrogenolysis processes, leading to the formation of hydrogenolysis and alkylation products.

Figure 1 gives the yields of pyrazines and accompanying products relative to the platinum content in the $Pt/Al_2O_3—In_2O_3$ catalyst. The formation of N-(β-hydroxypropyl)ethylenediamine and the dehydrogenation of piperazine to give pyrazine were examined. The pyrazine yield increases to some maximum with increasing platinum content and then remains unchanged or even drops. The yields of ethyl- and dimethylpyrazines as well as of high-boiling polyalkylpyrazines simultaneously increase. The formation of these products is attributed to hydrogenolysis of the starting reagents or intermediates and subsequent alkylation of the fragments of the pyrazine ring formed. Pyrrole is the product of incomplete deamination and an increase in the yield of this product also indicates an increase in hydrogenolysis at the C—N bond.

A clear example of the effect of hydrogenolysis on the formation of alkylpyrazines is found in the experiments on the dehydrodeamination of ethylenediamine on NiO—Al_2O_3 and NiO—SiO_2 (catalysts 10 and 11). The NiO—SiO_2 catalyst is characterized by more extensive reduction of NiO to metallic nickel [37]. Table 2 shows that, on one hand, decomposition of the starting diamine is enhanced (compare the yields of the catalyzate) and, on the other, the amount of alkylpyrazines formed is three times greater specifically on this catalyst. The capacity of metallic nickel to facilitate the alkylation of heterocycles including pyrazine has been demonstrated and even used for preparative purposes by Enomoto et al. [38].

Thus, the additives, which enhance the dehydrogenation function of the catalyst are the most efficient in the synthesis of pyrazines among the various additives used in modifying the Pt/Al_2O_3 catalyst. The simultaneous enhancement of the dehydrogenation activity and reduction in the acid function of the catalyst are especially favorable. This obtains, for example, upon modification using In_2O_3. The results obtained hold importance not only for selecting an active and selective catalyst for pyrazine synthesis but also for expanding our understanding of heteroaromatization pathways. It is most likely that the first reaction step is not cyclization (cyclodeamination or cyclodehydration), but rather dehydrogenation of the starting diamine or aminoalcohol. A negative consequence of an enhancement in the dehydrogenation capacity of the catalyst is the possibility of a simultaneous enhancement of the hydrogenolytic processes, leading to decomposition products, which alkylate the pyrazine ring to form polyalkylpyrazines. A wise choice of modifiers, increasing the dehydrogenation capacity and, at the same time, suppressing the hydrogenolysis at the C—N bond may enhance the selectivity of the catalyst in pyrazine synthesis.

EXPERIMENTAL

The experiments on the synthesis of pyrazine and methylpyrazine were carried out in a flow system with a vertical quartz reactor containing 17 cm^3 catalyst (1-2 mm). The catalyst sample was initially reduced by heating in hydrogen at 500°C and then, without interrupting the hydrogen flow, the reactor was cooled to the reaction temperature (300-400°C). The starting reagents were introduced with a volumetric rate of 0.35-1.0 h^{-1} with simultaneous dilution with hydrogen. The mole ratio of hydrogen to the starting reagent was 7:1 in the dehydrogenation of piperazine, (0.7-1.2):1 in the dehydrodeamination of ethylenediamine, and 1.3:1 in the dehydrocondensation of N-(β-hydroxypropyl)ethylenediamine.

In these experiments, we used a Pt/Al_2O_3 catalyst containing 0.6% platinum (catalyst 1) and a standard AP-64 industrial reforming catalyst with the same platinum content (catalyst 5). In addition, we studied Pt/Al_2O_3 catalysts modified by the addition of In_2O_3, Re_2O_7, CuO, and other oxides (catalysts 2-4 and 6), ZnO—Al_2O_3 samples with ZnO:Al_2O_3 mole ratio of 1:1 and 9:1 including samples modified by CuO (catalysts 7-9), and Al_2O_3—NiO and SiO_2—NiO samples containing 5% NiO (catalysts 10 and 11). All the additives except ZnO were introduced by impregnation of the support by the corresponding nitrate salts with subsequent roasting at 500°C. The Al_2O_3—ZnO samples were obtained by the joint precipitation of aluminum and zinc oxides from aqueous solutions of their nitrates using LiOH. The gels were washed to removed Li^+ ions, dried, roasted at 500°C, ground taking the fraction with 1-2 mm particle diameter, and impregnated by a solution of the salt of the corresponding modifier.

Piperazine, ethylenediamine, and N-(β-hydroxypropyl)ethylenediamine were used as the starting reagents. A commercial sample of piperazine was used without additional purification. Ethylenediamine was dehydrated prior to the experiments by heating at reflux over KOH. The aqueous layer was then removed, and the sample was distilled. The residual water content was 1.4%. A sample of N-(β-hydroxypropyl)ethylenediamine was obtained by mixing 3 moles ethylenediamine with 1 mole propylene oxide until the completion of the moderately exothermal reaction (2-2.5 h). The unreacted ethylenediamine was then distilled off at atmospheric pressure and the pure aminoalcohol was distilled at 115-120°C (15 mm Hg).

The reaction products were analyzed by gas-liquid chromatography with a flame ionization detector on a 2.7 m × 3 mm column packed with 5% PEG-20M on Inerton made basic with 0.9 mass % KOH. The helium gas carrier flow rate was 30 ml/min. The column temperature was initially 110°C and then raised gradually to 160 and 200°C.

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