Gas chromatographic analysis of the products of catalytic reduction of nitric oxide by ammonia

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The behavior of small amounts of nitric oxide in the presence of ammonia and excess oxygen on adsorbents of different textures was studied by gas chromatography. A scheme for the gas chromatographic analyses of the products of catalytic reduction of nitric oxide by ammonia and the catalytic oxidation of ammonia by oxygen was suggested. The scheme makes it possible to prevent chemical reactions between components of the gas mixture analyzed during the accumulation of the products and their analysis, to exclude the partial or complete adsorption of NO on microporous adsorbents, and to monitor the content of components at a level of 500 ppm and lower.

Key words: gas chromatography; nitrogen oxides, ammonia; interaction with adsorbents of various textures; analysis of small amounts.

To purify industrial waste containing NO, the reaction of its catalytic reduction by ammonia to molecular nitrogen is often used:[1–3]

$$4\ NH_3 + 4\ NO + O_2 = 4\ N_2 + 6\ H_2O \qquad (1)$$

The products of this process (Table 1) also contain N_2O and NO_2. It is rather difficult to analyze a mixture containing O_2, N_2, NO, N_2O, NO_2, NH_3, and H_2O. In addition, the existence of water, nitrogen dioxide, and unreacted ammonia does not exclude the formation of salts, for example, ammonium nitrate, during the analysis.

Only several publications concerning gas chromatographic analysis of these mixtures have appeared to date.[4,5] The known procedures of the gas chromatographic determination of the catalytic reduction of NO by ammonia[5] are imperfect from the viewpoint of quantitative analysis for many reasons. One of them is that the catalytic reduction of NO occurs, as a rule, in a medium with high content of oxygen. The procedure suggested in the previously published work[5] is designed for the determination of components of a mixture in the absence of oxygen, and the authors only suppose that its presence will not affect the results of the analysis. In addition, the determination of the substances indicated at a level of hundredths of a percent and lower using a heat-conductivity detector seems impossible without their preliminary concentration.

In this work, the procedure of gas chromatographic analysis, which allows one to take into account the factors preventing the quantitative determination of the components of the reaction mixture.

Table 1. Composition of the mixture analyzed

Component	Concentration (vol.%)
NH_3	0.01—0.05
NO	0.01—0.05
N_2O	0.01—0.1
NO_2	0.01—0.1
N_2	0.01—0.05
O_2	0.05—2.0
He	The rest

Experimental

The scheme of gas chromatographic analysis of the products of the catalytic reduction of NO by ammonia (Fig. 1) suggests, first, the separation of NH_3 and NO_2 from the mixture in a trap with water *8* and the separation of the mixture from water vapor using a trap *9* (43 cm×3 mm) packed with a special sorbent to capture water and elute the whole mixture without changes in its composition. The separation of O_2 and N_2 (total) and the accumulation of small amounts of NO are carried out at room temperature in the next trap *10* (50 cm×3 mm) containing copper sulfate cation-exchange resin as the adsorbent.[6] Oxygen and nitrogen, leaving traps *10* and *11* (total peak), get on a *16* column with the molecular sieve NaX (2 m×2 mm), where they are separated and registered by a heat-conductivity detector (*19*). Nitric oxide is accumulated on the copper sulfate cation-exchange resin, and N_2O is accumulated in trap *11* (35 cm×2 mm). The homogeneous microporous carbon-containing composite, which consists of the carbon fiber (actilene) (90%) and pseudoboehmite (10%),

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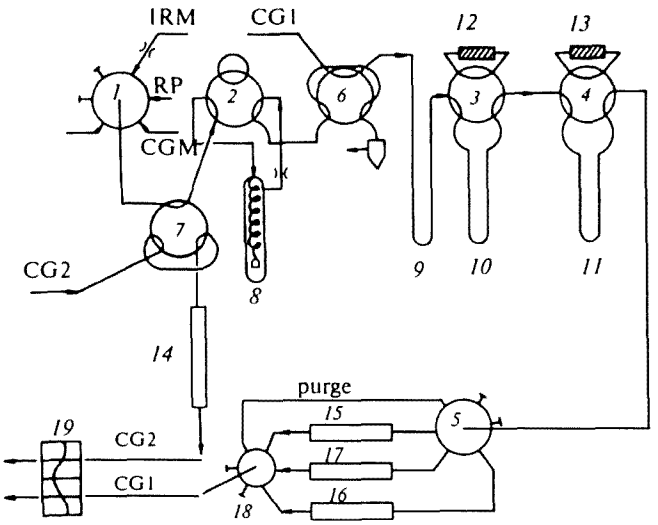

Fig. 1. Diagram of the gas chromatographic analysis of the products of the catalytic reduction of NO by ammonia: *1—5*, reverser valves; *6* and *7*, dosing valves; *8—11*, traps; *12* and *13*, resistances; *14—17*, gas chromatographic columns; *18*, switchgear; *19*, heat-conductivity detector; CG, carrier gas.

was synthesized and named actipseudoboehmite, to be used as the adsorbent for the accumulation of N_2O.[7]

After thermodesorption at 120 °C, N_2O and NO were analyzed on a *15* chromatographic column (1.5 m×3 mm) packed with Chromosorb-104 and on a *17* column (30 cm×2 mm) with copper sulfate cation-exchange resin, respectively (the temperature of the columns was 80 °C).

In the scheme presented, *12* and *13* are the special resistances to prevent disbalance of the line when the reverser valves *3* and *4* are reversed. The dosing valve *6* with a 3-mL loop serves to introduce a sample. In addition, the scheme designs the seven-way (six-position) reverser valve *5* for the consecutive connection of the chromatographic columns and injecting the sample through the switchgear *18* into the heat-conductivity detector *19*. The initial reaction mixture (IRM), reaction products (RP), and calibrating gas mixture (CGM) were injected by the seven-way (six-position) reverser valve *1*. In the cases when very small amounts of nitrogen should be fixed on the column with the molecular sieve NaX, oxygen, which is present in considerable amount and is eluted before nitrogen, is removed (completely or partially) by the chromium-nickel catalyst mounted in front of the column with NaX.

Ammonia and NO_2 (500 ppm and lower) were determined after they were accumulated in the trap with water by ion chromatography on a Tsvet 3006 chromatograph using a KRS-8P cation-exchanger and a KhIKS-1 anion-exchanger, respectively. In addition, the scheme allows for the possibility of the gas chromatographic analysis of ammonia using a *14* chromatographic column (1.5 m×2 mm) packed with the organic porous polymer Hayesep C, which was modified by 4.5 wt.% KOH, and provided with the dosing valve *7*.

The preliminary study of the chromatographic behavior of small amounts of NO on the sorbent in the presence and absence of oxygen was carried out on the setup presented in Fig. 1, changing the positions of traps *10* and *11* with the corresponding sorbents. This is caused by the fact that the copper sulfate cation-exchange resin is successfully used in the gas chromatographic analysis of NO, including the analysis of small amounts of it.[6] Such a change in the construction of the setup makes it possible to study the behavior of NO on adsorbents of different natures and adsorption textures.

To reveal the possible catalytic effect due to the adsorbents used for the accumulation and separation of the reaction mixture, special studies of their catalytic activity in reaction (1) were carried out on a flow-type setup, determining the degree of conversion of NO at different temperatures of the reactor.

The amount of the adsorbent-catalyst used in reaction (1) was 0.4 g, the mass flow rate of the reaction mixture was 10 L h^{-1}, and its composition was the following: NO, 500 ppm; NH_3, 500 ppm; and O_2, 0.5 vol.%. The activity of the adsorbent-catalysts was characterized by a first-order rate constant (k), which was calculated by the equation:

$$k = v/(g \cdot S) \cdot \ln 1/(1 - x)$$

where v/L h^{-1} is the mass flow rate of the reaction mixture; g/g is the weighted sample of the catalyst; S/m^2 g^{-1} is the specific surface area; and x is the degree of conversion of N_2O.

The volume of the sample, which can be passed through traps *10* and *11* before the passage of NO and N_2O, was estimated by the determination of adsorption dynamic capacities[8] of copper sulfate cation-exchange resin and actipseudoboehmite with respect to NO and N_2O. The specific retention volumes of these compounds ($V_{m,1}$) on the given adsorbents were determined at several temperatures. The values of the adsorption dynamic capacity of the adsorbents were determined by the extrapolation to the concentrating temperature (20 °C) of the dependence of the logarithm of the specific retention volume of the sorbate on the inverse absolute temperature.

Results and Discussion

A comparative study of the chromatographic behavior of small amounts of NO (0.05—0.1 vol.%) in the presence and absence of oxygen (helium as the diluting gas) was performed on the setup specially modified for this purpose (see Experimental).

It was shown that in the absence of oxygen, NO passes freely through the column-trap *11* packed with the microporous adsorbent (Fig. 2, *a*), which is mounted in front of trap *10* with the copper sulfate cation-exchange resin. The addition of O_2 (~1—2 vol.%) to the mixture results in the complete adsorption of NO on the microporous adsorbent. This results in the absence of the peak of NO on the chromatogram (Fig. 2, *b*). This result can also be useful for the solution of problems associated with the room-temperature purification of various gaseous media, *e.g.*, N_2O used in medicinal practice, from NO traces.

The partial (20—50%) absorption of NO in the presence of oxygen also occurs on the organic porous polymer Hayesep C packed into the column-trap *11* instead of actipseudoboehmite. The deposition of, *e.g.*, polyethylene glycol (20 wt.%, molecular mass 15000) on the

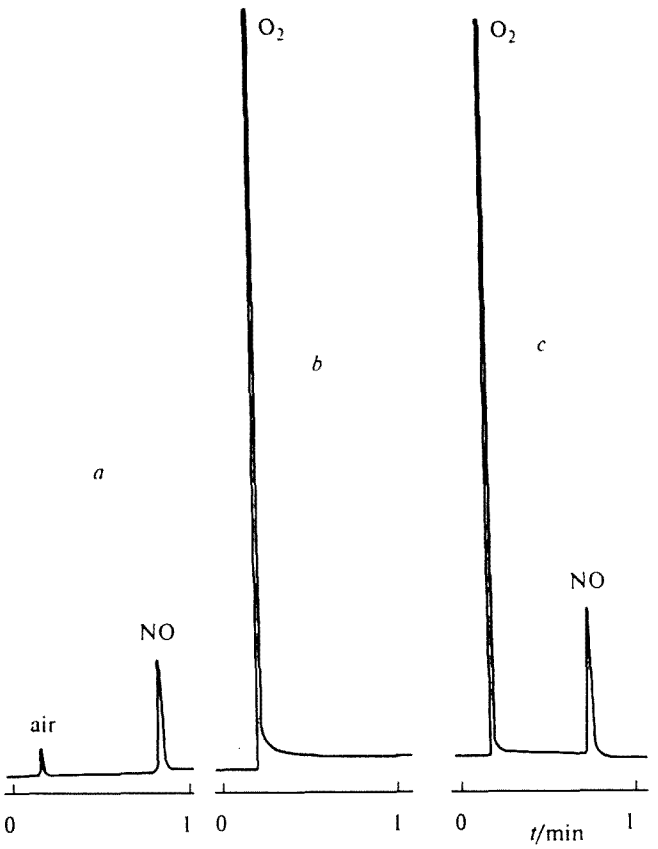

Fig. 2. Chromatograms obtained on the column with the copper sulfate cation-exchange resin (the temperature was 80 °C, the mass flow rate of the carrier gas was 30 mL min^{-1}): *a*, mixture of NO (400 ppm) and helium after its passage through the column-trap with actipseudoboehmite; *b*, mixture of NO (500 ppm) and helium in the presence of excess oxygen (approximately 2 vol.%) after its passage through the column-trap with actipseudoboehmite; *c*, mixture of NO (500 ppm) and helium in the presence of excess oxygen after its passage missing the column-trap with actipseudoboehmite.

organic porous polymer Polysorb-1 provides free elution of NO, which is present in helium along with excess oxygen, through the given packing agent without any change in the quantitative composition of the mixture.

When the mixture of NO and O_2 is injected to the column-trap with the copper sulfate cation-exchange resin, missing the column-trap packed with the microporous carbon-containing adsorbent, the peak of NO does not disappear (see Fig. 2, *c*).

The presence or absence of oxygen in the mixture exerts no effect on the gas chromatographic behavior of N_2O.

This behavior of small amounts of NO in the presence of oxygen on the adsorbents studied is likely caused to a great extent by micropores. In fact, NO and oxygen are not separated on carbon adsorbents and organic porous polymers, and the chemical interaction of NO with O_2 is facilitated in the presence of micropores, whose adsorption potential is great. This results in the formation of the reaction product, which is chemically bound with the surface, probably NO_2. This especially concerns microporous adsorbents and, in particular, actipseudoboehmite used in this work.

The deposition of the stationary liquid phase (20 wt.%), for example, polyethylene glycol 15M, on Polysorb-1 results in primary filling of micropores of the polymer and creation of the liquid phase film in which the solubility (and hence, contact time) of NO and O_2 decreases sharply and no chemical interaction occurs.

Additional studies were necessary for this reaction mixture, which is sensitive to the adsorption texture of the adsorbents used for its separation. It was also reasonable to study the behavior of the adsorbents as the possible catalysts for reaction (1) during the chromatographic analysis of this reaction mixture. Carbon-containing adsorbents were used for this purpose, because some of them are applied in the gas chromatographic analysis of NO[9] and as carriers for preparation of catalysts for reaction (1).[10] Their thermal stability makes it possible to perform catalytic studies in a wide temperature range. These carbon materials are characterized by different adsorption textures and different mutual orientations of hexagonal carbon layers in their nanotextures.[7] The surface of the adsorbents used is mainly formed by either basic facets of the graphite crystal structure (graphitized thermal carbon black (GTCB)[11]) or their edges (catalytic filamentary carbon obtained by the catalytic methane decomposition on nickel (KFU-I) and copper-nickel (KFU-II) catalysts[7]) as well as by the partially ordered carbon structure (carbon fiber actilene[12] and actipseudoboehmite synthesized from it[7]). The values of the specific surface and volume of micropores, which primarily characterize the adsorption texture of these adsorbents, are presented in Table 2.

Our studies showed that the adsorbents studied are inactive in reaction (1) up to 225 °C and almost all of them are active at 400 °C. According to the data of

Table 2. Degrees of conversion and rate constants (k) of reaction (1) on carbon sorbents of different nanotextures

Adsorbent-catalyst	Weighted sample/g	S_{sp} /m^2 g^{-1}	$g \cdot S$ /m^2	Degree of conversion, x (%)	k /m^{-2} h^{-1}	V_{micro} /cm^3 g^{-1}
GTCB	0.4	10	4.0	0	0.0	0.0
Actilene	0.4	790	316.4	11	$3.68 \cdot 10^{-3}$	0.31
Actipseudoboehmite	0.4	1030	412.0	58	$2.10 \cdot 10^{-2}$	0.43
KFU-II	0.4	118	47.2	12	$2.73 \cdot 10^{-2}$	0.007
KFU-I	0.4	117	46.8	39	$1.06 \cdot 10^{-1}$	0.0

Table 2, the carbon adsorbents exhibit different activities in reaction (1). The catalytic activity is determined to a great extent by the mutual orientation of hexagonal carbon layers in their nanotexture rather than by the adsorption texture. For example, the rate constant (k) for reaction (1) is maximum for KFU-1 and KFU-11, whose surfaces are formed by edge facets of the graphite crystal structure, while their adsorption texture virtually does not contain micropores.

The graphitized thermal black is inactive in this reaction, because its surface is composed of basic facets of the graphite crystal structure and the adsorption texture has almost no micropores, like those of catalytic carbon materials.[11]

For the carbon fiber actilene, whose surface is formed by the partially ordered carbon structure and micropores 0.31 $cm^3 g^{-1}$ in volume (see Ref. 7), the k value is almost one order of magnitude lower than those for KFU-1 and KFU-11.

An additional mechanical activation of actilene during the synthesis of actipseudoboehmite results in a greater ordering of the carbon structure of the latter and an increase in the volume of micropores. For example, the value of the degree of graphitization is 0.50 for the composite compared to 0.28 for the initial actilene, and the volume of micropores is equal to 0.43 $cm^3 g^{-1}$ for the material obtained. As a result, the rate constant for reaction (1) for actipseudoboehmite is 5.7-fold higher than that for the initial actilene (Table 3).

Thus, the experiments performed showed that several requirements should be fulfilled for the determination of small amounts of NO in the presence of oxygen.

Therefore, the scheme of the analysis presented in Fig. 1 was used in the work. This scheme makes it possible to exclude the chemical interaction of components of this reaction mixture. Passing the mixture through the trap with water removed ammonia and NO_2 from the mixture and, on the one hand, the formation of salts was prevented during the gas chromatographic determination of the products of reaction (1), while on the other hand, they were accumulated for the analysis by ion chromatography (see Figs. 3 and 4). It is very important to remove ammonia from the mixture, because it modifies any sorbent in the chromatographic column, transforming it to the catalyst for reaction (1).[13] Therefore, when ammonia should be analyzed by gas chromatography, the scheme provides the use of the chromatographic column CC (1.5 m × 2 mm) with the organic porous polymer Hayesep C, whose surface is covered by KOH (4.5 wt.%). The examples for this analysis on the initial (a) and KOH-modified (b) samples of the polymer are presented in Fig. 5, which are evidence for the advantages of the latter in the analysis of small contents of ammonia (800 ppm and lower).

The use of trap 9 packed with Polysorb-1 modified by diglycerol (20 wt.%) makes it possible to capture the

Table 3. Specific retention volumes of NO and N_2O on the copper sulfate cation-exchange resin at various temperatures

T/°C	$V_{m,1}$/mL g^{-1}	
	NO	N_2O
50.5	118.0	14.0
61.0	49.0	9.6
71.0	30.0	7.1
89.0	13.5	5.1
99.6	9.1	3.7
(20)	765.0	38.1

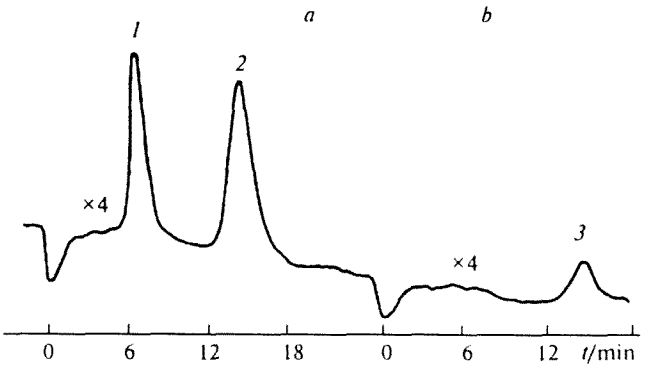

Fig. 3. Chromatograms of the standard solution (a) (1, 2, 0.1 mg mL^{-1} NO_2^- and NO_3^-, respectively) and nitrogen dioxide obtained in the catalytic reduction of NO by ammonia (b) (3, NO_3^-, $1.9 \cdot 10^{-6}$ wt.%) on the column (3×200 mm) with the KhIKS-1 anion-exchange resin.

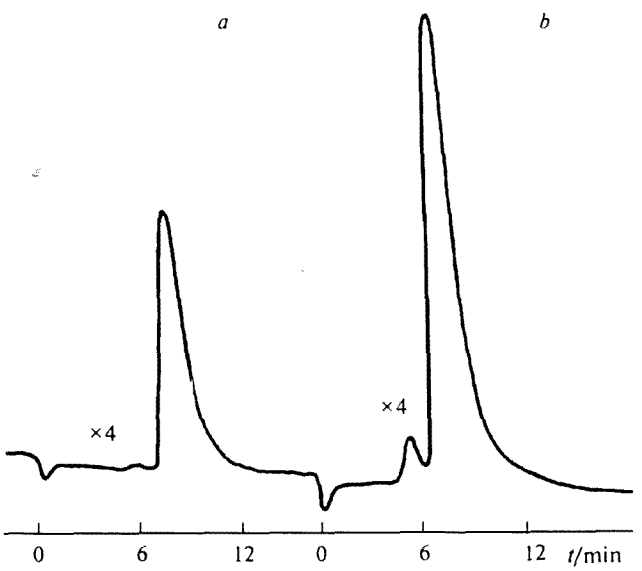

Fig. 4. Chromatogram of ammonia obtained on an ion chromatograph using the column (3×200 mm) packed with the KRS-8P cation-exchange resin: a, standard solution (NH^+, 0.01 mg mL^{-1}) and b, initial reaction mixture (NH^+, 0.05%) after its accumulation in the trap with water.

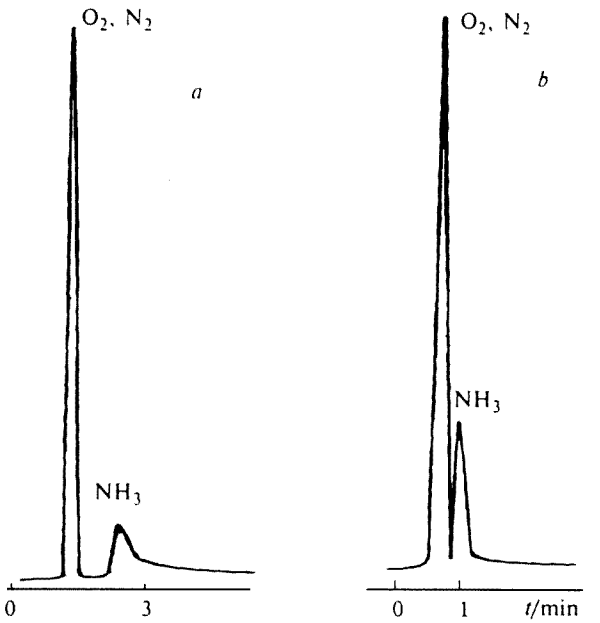

Fig. 5. Chromatograms of ammonia (800 ppm) obtained on the column with nonmodified (*a*) and modified 4.5 wt.% KOH Hayesep C (*b*) (T_{col} = 80 °C).

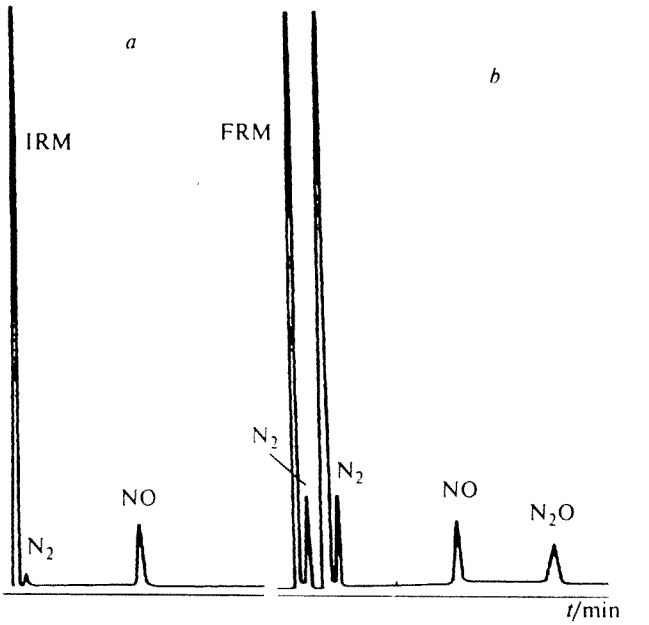

Fig. 6. Chromatograms of the initial reaction mixture (IRM) containing NO (590 ppm) (*a*) and of NO, N_2O, and N_2 entering the composition of the final reaction mixture (FRM) and formed in reaction (1) after their accumulation from two samples (*b*).

water vapor coming from the trap with water.[14] NO, N_2O, O_2, and N_2 are eluted from the modified polymer without changing the composition of the mixture, because the modification used the amount of diglycerol necessary, as shown above, for filling micropores of Polysorb-1 and free passage of NO in the presence of excess O_2, and not only for the retention of water. It is necessary to retain water in trap *9*, because when it gets into trap *10* with the copper sulfate ion-exchange resin, it decreases considerably the adsorption capacity of the latter with respect to NO (training of the trap with this sorbent at 100 °C in the carrier-gas flow restores it to its former level).

Entering trap *10* with the copper sulfate cation-exchange resin, NO is trapped with it, while O_2, N_2, and N_2O get into the next trap, *11*, with actipseudoboehmite, where N_2O is captured. Then oxygen and nitrogen are separated in the chromatographic column *16* with the molecular sieve.

When oxides NO and N_2O are accumulated in sufficient amounts, they are analyzed in turn (in the absence of oxygen) on column *15* with Chromosorb-104 and on column *17* with the copper sulfate cation-exchange resin, respectively.

The value of the sample necessary for accumulating the amounts of nitrogen oxides on actipseudoboehmite and on the copper sulfate cation-exchange resin, which are required for detection by the heat-conductivity detector, were estimated by determining the adsorption dynamic capacity of the latter. The specific retention volumes of NO and N_2O on the copper sulfate cation-exchange resin at several temperatures and the values of the adsorption dynamic capacity $V_{m,l}$ (20 °C) determined by the concentrating (room) temperature of the plot of the dependence of the logarithm of the specific retention volume of NO or N_2O on the inverse absolute temperature are presented in Table 3. As seen from Table 3, the $V_{m,l}$ value (20 °C) for NO on the copper sulfate cation-exchange resin is approximately one order of magnitude higher than that for N_2O and is equal to 765 mL g^{-1} (for NO). By contrast, N_2O is retained more strongly on the microporous adsorbent, and therefore it is accumulated in trap *11* filled with it. The $V_{m,l}$ value for N_2O on actipseudoboehmite is equal to 370 mL g^{-1}.

The order of traps *10* and *11* in the scheme suggested (see Fig. 1) is explained by the fact that when the order changes to the opposite one, as shown above, the irreversible chemisorption of NO in the presence of oxygen on actipseudoboehmite occurs. When it is necessary to accumulate nitrogen oxides NO and N_2O in the absence of oxygen, the trap-concentrator can be used, which is composed of 60% copper sulfate cation-exchange resin retaining NO more selectively, and 40% actipseudoboehmite retaining selectively N_2O. This makes it possible to obtain the retention of these substances within one order of magnitude. For example, the specific retention volume of NO at 50 °C on the composed column (35 cm×2 mm) is equal to 91 mL g^{-1}, while that of N_2O is equal to 64 mL g^{-1}.

The $V_{m,l}$ values (20 °C) determine the limiting volume of the sample, which can be passed through the given amount of the adsorbent before the passage of the component to be trapped. The variation of the amount of the adsorbent makes it possible to select the volume of the sample necessary to provide the required sensitivity of the detector.

One of the chromatograms for determining N_2, NO, and N_2O formed in catalytic reaction (1) after their accumulation from two samples (Fig. 6, *b*) is shown in Fig. 6 (the contents of NO, N_2O, and nitrogen are equal to 280, 67, and 160 ppm, respectively). The chromatogram of the initial mixture is shown in Fig. 6, *a* (the content of NO is 590 ppm).

The scheme of the chromatographic analysis suggested is rather universal and can be used not only for analyzing the products of the catalytic reduction of NO by ammonia, but also for analyzing the products of the catalytic synthesis and oxidation of ammonia.

The balance calculated with respect to NO and NH_3 for the catalytic reduction of NO by ammonia and the catalytic oxidation of ammonia by oxygen was 80—98%, and the minimum contents of nitrogen oxides and ammonia, which can be determined in these reactions, were 15—20 ppm.

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