Physicochemical Processing of Human Exometabolites for Closed Life Support Systems

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Abstract

Composition of gas mixtures formed during the electrochemical (in the presence of H_2O_2) oxidation of the wastes of human vital activities and subsequent decomposition of carbamide remaining in solution after the oxidation of metabolites was studied. A principal possibility of the selective catalytic oxidation of ammonia evolved due to the decomposition of carbamide to form nitrogen oxides was demonstrated, for the purpose of obtaining the salts of nitric acid those are well assimilated by plants.

Key words: life support system, processing exometabolite processing, catalytic ammonia oxidation, nitrogen oxides

INTRODUCTION

By present, a significant progress is attained in the development of life support systems (LSS) for an extended staying of humans within circumterrestrial space stations. However, such systems involve a large amount of non-reprocessible wastes, which could cause great problems related to the conservation and storage of the wastes. Using the biological methods for the oxidation of a number of wastes is unacceptable because of incompatibility of the accumulation and processing rate in the restricted space of the station. Integrating the physical, chemical and biological methods of waste treatment and their subsequent involving in the mass transfer process could to a considerable extent provide the completeness of such a biotechnical system.

Known physicochemical processes for oxidation of human life activity wastes (dry and wet mineralization) are difficult to integrate into biological life support systems.

This could be connected with mismatching the parameters of waste recycling process (temperature, pressure, deleterious nature of the media) and the conditions the natural human habitat, as well as with the inability to involve a number of products of physicochemical processing into the biological turnovers. So, in the case of dry mineralization which includes combusting the dried waste within the temperature range of 800−1250 K, in addition to the CO_2, furnace gases are produced containing components (CO, SO_2, NO_2, dioxin) hazardous for humans and plants [1]. In the case of wet mineralization based on heating wastes in the atmosphere of oxygen under high pressure, the formation of salt sediments on the walls and internal surfaces of the equipment occurs, as well as leaching of heavy metal ions (Cr^{3+}, Cr^{6+}) is observed those are hazardous with respect to humans even at low concentration values. Other physicochemical methods of recycling the waste using ozone, hydroxyl radicals, and ultraviolet radiation as oxidants have not found yet any practical applications being of theoretical interest only.

A fundamentally novel physicochemical method for processing vegetable waste and human exometabolites that consists in the waste oxidation in the media of 30 % H_2O_2 solution under the action of electric current was developed at the Institute of Biophysics of the SB RAS [2–4]. The experimental studies demonstrated that there is the possibility of using this method for the involving the products of processing into the internal mass transfer cycles inherent in a biological life-support system [5–7]. After this treatment, in solution after electrochemical oxidation there are carbamide (in the course of oxidation up to 20 % of carbamide could decompose) and a number of mineral salts remaining, those are suitable for plant growth [8]. In addition, a gas is evolved, whose chemical composition is not determined yet.

The carbamide remained in the solution should be decomposed, since its presence in a closed life support system promotes the emergence and spreading of pathogenic bacteria. In turn, it shouldn't be allowed that the atmosphere of the life support systems with humans contained any ammonia species of nitrogen and other toxic compounds those could be formed *via* the electrochemical oxidation of exometabolites and the subsequent degradation of carbamide. Ammonia could be oxidized using different heterogeneous catalysts to yield the oxides of nitrogen followed by the preparation of nitric acid salts those can readily absorbed by plants. Platinum grids represent the most active catalyst for the ammonia oxidation those operate stably under industrial conditions at high temperature values and a high flow rate of supplying ammonia-air mixture, as well as at ammonia concentrations over 3 % [9]. In the system under investigation, there is a irregular gas evolution observed, thus the ammonia concentration in the gas mixture changes. In this regard, it is obvious that selective ammonia oxidation catalysts are required those could operate within a wide range of conditions and the concentration of impurities. As the examples of such catalysts, researchers could use both bulk oxide and supported catalysts developed at the Institute of Catalysis of the SB RAS (Novosibirsk) [10–12].

The aim of this work consisted in determining chemical composition of the gas mixture

formed at different stages of processing LSS wastes (electrochemical oxidation, carbamide decomposition) for the presence of possible toxic (unwanted) compounds among the reaction products and the development of methods for processing them with involving in an intrasystem turnover.

EXPERIMENTAL

Oxidation of organic wastes

Figure 1 demonstrates the setup for the "wet" combustion of organic wastes. A suspension of powdered solid and liquid exometabolites of humans in 30 % H_2O_2 medium was subjected to alternating electric field through carbon electrodes. On average, the oxidation of 1 g of dry straw, cellulose, and lignin required for consuming 16–18 mL of 30 % H_2O_2 solution, whereas oxidizing 1 g of solid human exometabolites required for 4 mL, 1 mL of urine required for 0.5 mL of 30 % H_2O_2. The gas evolved in the tubes was supplied through a system of tubes to NH_3 trap which represented a flask with the solution of carbonic acid, filled with glass tube scrap to increase the time of passing the of gas through the solution. The trap temperature was equal to 4 °C. Owing to the use of H_2CO_3, ammonia was bound in the form of ammonium carbonate for the purpose of its easy isolation for the subsequent nitrifi-
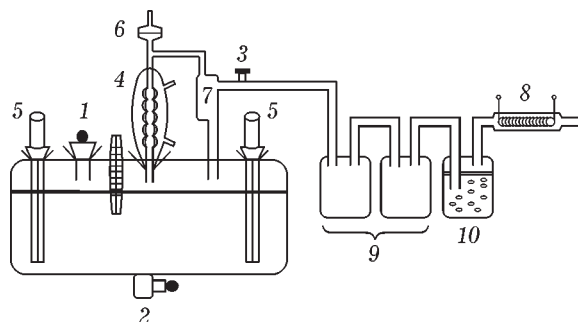

Fig. 1. Scheme of the setup for the wet combustion of organic wastes in the environment of H_2O_2 under the action of alternating electric field: *1* – cover for pouring-in H_2O_2 and wastes, *2* – drain valve, *3* – valve, *4* – gas cooling coil, *5* – electrodes, *6* – membrane for foam separation, *7* – capacity for gathering excess foam, *8* – platinum catalyst of hydrogen oxidation, *9* – vessels for collecting gases, *10* – vessel with H_2CO_3 solution.

cation. After absorbing ammonia, the gas was additionally passed through the platinum catalyst heated up to 200 °C. In this case, hydrogen formed due to the electrochemical decomposition of exometabolites was oxidized by oxygen from the gas phase to form water and then it was taken into gas holders. The completion of the reaction was judged by the clarifying the solution and ceasing the gas evolution, the reaction duration amounted to 2.53 h. The technique used and the composition of the resulting solution were described in detail in [2].

Decomposition of carbamide

In order to determine the kinetics of carbamide decomposition by means of urease we conducted two types of experiments.

In the experiment No. 1, to 250 mL of an aqueous solution of carbamide (carbamide content 5 g/L) was added 2.5 g of urease, the mixture was bubbled with air. In order to determine the kinetics of carbamide decomposition the reaction temperature was varied from 37 to 67 °C, the rate of air bubbling through the solution (V) was varied from 13.2 to 32.4 L/h. The composition of the gases leaving the reactor was analyzed by means of infrared spectroscopy.

In the experiment No. 2, to a solution formed in the course of the oxidation of organic wastes was added an extract of soybean containing the enzyme of urease, 5 g of the extract per 1 L of the solution. The gas released during the reaction at 37 °C, circulated during 1 day through a mineral solution with urease and through carbonic acid solution to fix the ammonia (Fig. 2) at a rate of 1−2 L/min. After the experiment, the gas was collected in the gasholder for subsequent analysis. According to the calculations, the amount of ammonia produced during the conversion of 1 L exometabolite mixture should be equal to about 8.9 L.

Ammonia oxidation

The reaction of ammonia oxidation into nitrogen oxides was carried out using a quartz flow-through reactor with the diameter of 5 mm at the temperature ranging within 250−900 °C. Catalysts were investigated as a 0.25−
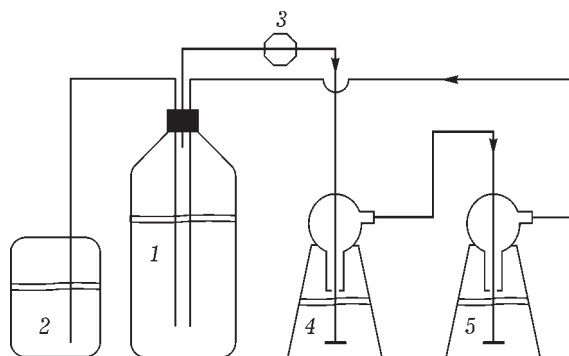

Fig. 2. Scheme of carbamide decomposition unit: *1* − gas holder with gas from the reactor; *2* − tank with water to equalize the pressure inside the gas holder; *3* − pump for gas pumping; *4* − mineral solution with urease for decomposing carbamide; *5* − carbonic acid solution for ammonia fixation.

0.50 mm fraction, the total volume of the fraction was equal to 0.2 mL. The mass of the catalyst sample portions was equal to 0.143 g for 1 % $Pt/CeZrO_2$ and 0.192 g for IC 42-1 catalysts. The initial reaction mixture containing 1 % NH_3 or 1 % NH_3 + 0.5 % CO_2 in the air was supplied at a rate of 0.3 L/min, which provided the value of contact time equal to 0.025 s (under normal conditions). The composition of the final reaction mixture (NH_3, NO, NO_2, N_2O, H_2O, CO_2) was determined by means of an Infralum FT-801 FT-IR spectrometer (Russia) in an on-line mode. The accuracy of the analysis was equal to 5 %.

In the course of the experiments, we determined the conversion level of ammonia $X(NH_3)$ and CO_2, the reaction selectivity level for N_2O and NO ($S(N_2O)$ and $S(NO_x)$, respectively) calculated from the sum of products NO + NO_2, since under the conditions of the analysis the NO can be readily oxidized by atmospheric oxygen to produce NO_2.

Analysis of the gas composition

Determining the composition of the gas mixture collected in gas holders was performed using the method of gas chromatography. We used several columns: 1) NaX (2 m × 3 mm, T = 65 °C) to determine H_2, O_2, N_2, CH_4, CO; 2) Porapak N (3 m × 3 mm, T = 95 °C) to determine CO_2, NH_3, H_2O; 3) Carb 20M

(20 m × 0.22 mm, T = 60−180 °C) and Silica PLOT (15 m × 0.32 mm, T = 100 °C) for the determination of C_2−C_6 hydrocarbons, alcohols and aldehydes; 4) HP1MS (30 m × 0.32 mm, T = 40−220 °C, 2 °C/min) to determine the H_2S, SO_2, mercaptans.

The detection limit for NH_3 was equal to 0.3 %, for CH_4 100 ppm, for CO 100 ppm, for C_2−C_6 hydrocarbons 10 ppm, for sulphur compounds (H_2S, SO_2, mercaptans) 1 ppm.

The formation of H−C≡N after the reaction of ammonia oxidation in the presence of CO_2 was judged by the presence of absorption band at 2089 cm^{-1} in the IR spectra of the gas mixture [13, 14]. For the derivatives of cyanic acid R−C≡N (R = NH_4, CH_3, *etc.*), this band is shifted to 2220−2270 cm^{-1} overlapped with intense characteristic bands of CO_2 (2270−2400 cm^{-1}) and N_2O (2150−2260 cm^{-1}). In this connection, we performed a further qualitative analytical determination of cyanic acid derivative compounds [15]. For this purpose, through a flask filled with 40 mL of distilled water was passed a gas mixture after the reactor during 4 h. To the solution obtained was added 0.5 mL of KOH (3 mol/L) and 1 mL of 5 % of ferrous sulphate solution ($FeSO_4 \cdot 7H_2O$) and was boiled for 30 min. After that, to the solution was dropwise added a 10 % solution of hydrochloric acid up to obtaining an acidic medium and several drops of 5 % ferric chloride aqueous solution ($FeCl_3$). In the presence of 20−30 µg HCN in 1 mL of the sample there appears green or blue colour of the solution. When the HCN content is greater than 30 µg, blue precipitate of Prussian blue, that is a mixture of iron (II) hexacyanoferrates ($KFe[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$) is observed to appear.

The determination isocyano group N=C=O was performed according to the presence of the absorption band within the range of (1450−1400 cm^{-1}).

RESULTS AND DISCUSSION

Composition of the reaction products from the electrochemical oxidation of exometabolites

In the gas mixture collected after occurring the "wet" combustion of organic wastes in H_2O_2 environment under the action of passing over a platinum catalyst and of the alternating electric current, we found mainly oxygen (62.53 %), molecular nitrogen (33.39 %), water (~2.5 %), carbon dioxide (0.99 %), ammonia (0.47 %) and methane (0.12 %) (Table 1). We also detected trace amounts (less than 10 ppm) of organic compounds containing the CH_2 group (hydrocarbons, alcohols, aldehydes). The content of other compounds such as CO, H_2S, SO_2, mercaptans in the gas mixture was below the detection limit (1 ppm). As applied to LSS, the mixture contains an unacceptably high amount of ammonia, so the mixture is appropriate to be fed directly to the gas channel in order to mix it with the gases those evolve in the course of carbamide decomposition.

TABLE 1

Composition of gas emissions from the reactor under the wet combustion calculated per 1 L of the solution combusted

Compounds	Composition of the gas mixture after different stages of exometabolite processing, %	
	Wet combustion and passing through the Pt catalyst (working volume 17.716 L)	Decomposition of $CO(NH_2)_2$ and fixation of NH_3 (exp. No. 2, working volume 20.705 L)
O_2	62.53	53.50
N_2	33.39	28.57
CH_4	0.12	0.10
CO_2	0.99	15.33
NH_3	0.47	−
H_2O	2.50	2.50

Decomposition of carbamide

In the preliminary experiments, we found that in the course of the electrochemical reaction proceeding in the reactor only about 20 % of carbamide is oxidized. The resulting ammonia to a considerable extent is dissolved in the mineral solution obtained (~1660 mg/L). For performing the decomposition of carbamide, as an enzyme we used urease extract (hydrolytic enzyme from the group of amidases) derived from soybean flour. The latter could be produced in a closed life support system as a part of the phototrophic unit. The decomposition of carbamide in the presence of urease occurs due to the hydrolysis according to the equation

$$H_2N-CO-NH_2 + H_2O \rightarrow 2NH_3 + CO_2$$
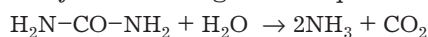
The mixture of ammonia and CO_2 produced in the course of the reaction could be immediately directed to a selective ammonia oxidation catalyst. However, in order to determine the conditions of the ammonia oxidation one needs for the information about the reaction kinetics of carbamide decomposition by urease and the exact composition of the reaction products after this stage.

Figure 3, a presents data concerning ammonia and CO_2 concentration depending on time (excluding the contribution of CO_2 present in the air) after adding urease to the aqueous solution of carbamide at 37 °C and the air flow rate equal to 13.2 L/h. It is seen that approximately in 25 min after starting the reaction an almost constant gas evolution is established, but the concentration of the reaction products is small. According to the estimations, the complete decomposition of carbamide at this temperature would require more than 80 h, thus the duration of such a process is unacceptable. A slight increase in the rate of releasing the products into the gas phase was observed with increasing the concentration of urease. A direct correlation between the rate of air bubbling through the solution and the concentration of the reaction products (see Fig. 3, b), as well as increasing the pH level in the solution as the reaction progresses indicate that the ammonia (mostly) and CO_2 resulting from the decomposition of carbamide are strongly dissolved in water.

A significant increase in the rate of gas evolution occurs with increasing the temperature of the reaction (see Fig. 3, c). However, choosing the conditions of carbamide decomposition requires taking into account the fact that at the temperature values higher that 60 °C (beginning the protein structure denaturation) the urease activity level begins to decrease.

It is also necessary to investigate the influence of in CO_2 and other trace impurities those present the gas phase resulting from the de-

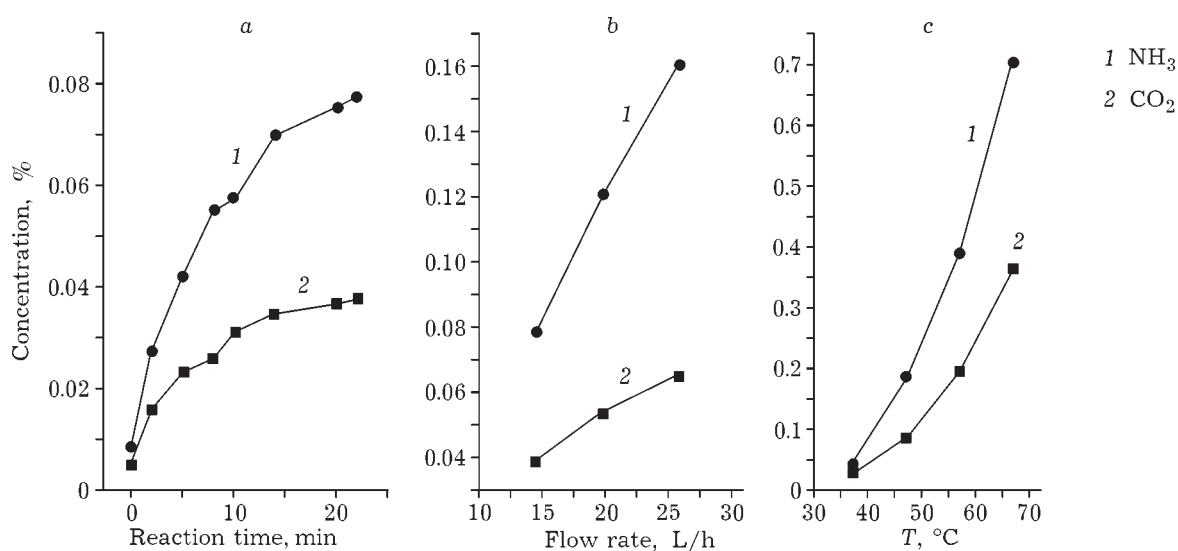Fig. 3. Kinetics of decomposing the aqueous solutions of carbamide with urease: a − the concentration of NH_3 and CO_2 depending on time (T = 37 °C, V = 13.2 L/h); b − the influence of solution air-bubbling at T = 37 °C upon the quasi-steady-state values of NH_3 and CO_2 concentration; c − an effect of the solution temperature (V = 32.4 L/h) on the reaction rate (the concentration valued of the reaction products in 2 min after the starting the reaction).

composition of carbamide, upon the catalytic ammonia oxidation.

The analysis of the composition of gaseous reaction products after the experiment No. 2 demonstrated that the main products are presented by ammonia which under the recycle conditions was almost completely removed in the form of $(NH_4)_2CO_3$, and carbon dioxide (see Table 1). In addition, the gas phase contains methane in small amounts (0.10 %), whereas the content of C_2-C_6 hydrocarbons, alcohols and aldehydes under the limit of detection. As applied to the LSS, the mentioned organic compounds should be removed from the mixture *via* passing the gas through a catalytic furnace, where they will be oxidized to give water and CO_2. To provide for the oxidation process is very important because under the conditions close to those under the ammonia oxidation, the reaction between methane and ammonia to form HCN on platinum is quite possible in principle to occur [16]. In the case of such realizing the stage of carbamide decomposition, the ammonia bound in the form of ammonium carbonate could be readily isolated *via* heating the latter above 60 °C with forming a mixture with a preset concentration of ammonia for subsequent nitrification.

Ammonia oxidation

For ammonia oxidation we suggested to use the following catalysts: 1) cerium-zirconium oxides supported platinum catalysts (1 % Pt/ CeZrO$_2$); 2) bulk iron oxide catalyst IC-42-1 developed at the Institute of Catalysis of the SB RAS currently used for the ammonia oxidation as a second step after platinoid grids. In order to determine the conditions of the process (100 % conversion of ammonia, the formation maximum NO amount, minimum N_2O content) we investigated the activity of these catalysts with respect to model gas mixtures. In the course of carbamide decomposition, carbon dioxide is released, so we carried out experiments to elucidate CO_2 effect on the activity and selectivity of catalysts.

Figure 4, *a* demonstrates the conversion level of ammonia $X(NH_3)$ and the selectivity level with respect to N_2O and NO_x (S_{N_2O} and S_{NO_x}, respectively) depending on the reaction temperature in the case the supported 1 % Pt/CeZrO$_2$ catalyst. It is seen that the catalyst begins to actively oxidize ammonia already at the temperature amounting to about 300 °C, whereas the major products under these conditions are presented molecular nitrogen and nitrogen monoxide ($S(N_2O) = 15$ %). However, the intense formation of N_2O passes through a maximum and decreases with increasing the temperature. With increasing the temperature, an increase in the selective formation of nitrogen oxides (NO and NO_2) is observed. At moderate temperature values (500−600 °C), the yield of nitrogen oxide reaches a maximum of about 83 %.

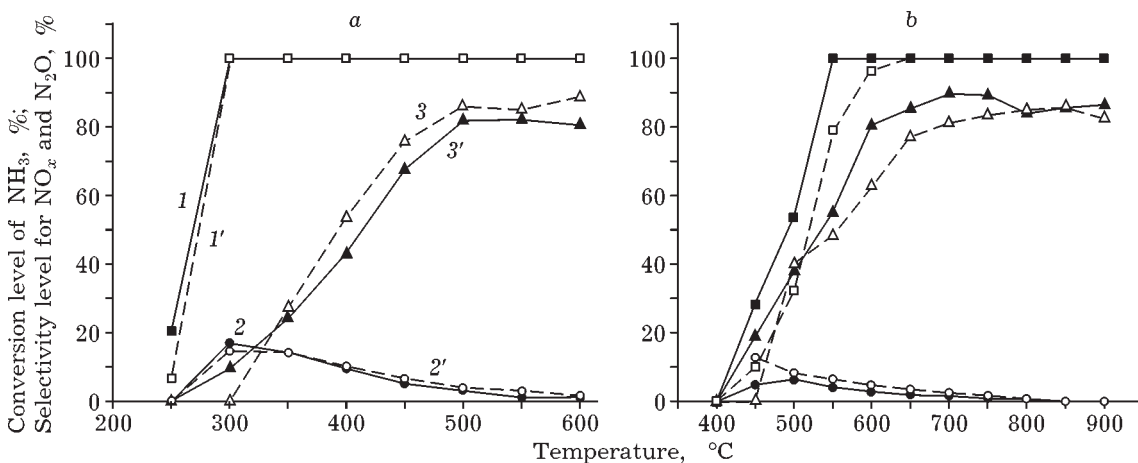We have found that the bulk oxide catalysts are less active in the reaction of ammonia

Fig. 4. Conversion level of ammonia (*1, 1′*) and selectivity for nitrogen oxides NO_x (*2, 2′*) and N_2O (*3, 3′*) depending on the reaction temperature for different catalysts: *a* − 1 % Pt/CeZrO$_2$, *b* − IC-42-1 in the reaction of ammonia oxidation with no CO_2 added (*1−3*) and in the presence of 0.5 % CO_2 (*1′−3′*).

oxidation. So, on the IC-42-1 iron oxide catalyst, the reaction starts at a higher temperature value, and the complete conversion of ammonia can be reached at about 550 °C (see Fig. 4, *b*). The maximum yield of nitrogen oxides is achieved at 650−750 °C amounting to about 89 %. Within the temperature range of 800−900 °C, a slight decrease in the selectivity with respect to NO_x is observed, to all appearance, due to the formation of molecular nitrogen. The maximum selectivity with respect to N_2O on the iron oxide catalysts is observed at 450−500 °C being equal to about 6 %.

We have investigated the influence of the addition of carbon dioxide upon the activity and selectivity of the catalysts in the reaction of ammonia oxidation (see Fig. 4). It is seen that the addition of 0.5 % CO_2 ($NH_3/CO_2 = 2$) to the initial reaction mixture exerts almost no effect on the process. A slight decrease in the conversion level of ammonia is observed at low temperature values (250−500 °C), which could be caused by a competitive adsorption of NH_3 and CO_2 on the catalyst surface. The observed discrepancies in the activity and selectivity of catalysts in the reaction of ammonia oxidation in the presence of CO_2 at high temperature values could be attributed to an experimental error.

In the course of the experiments, we carried out monitoring the changes in carbon dioxide concentration in order to determine its possible transformations on the catalysts. It has been found that the change in the concentration of CO_2 with respect to the initial concentration in the reaction mixture ranged within 5 % for all the experiments being within the accuracy of the analysis for CO_2. The IR spectra demonstrated no absorption bands at 2089 and 1450−1400 cm^{-1}, those are characteristic of the stretching vibrations of the HCN molecule and isocyano groups (N=C=O), respectively. The qualitative analytical determination of the derivative compounds of cyanic acid via hydrolysis and determining CN groups by means of the characteristic reaction with iron salts [12] demonstrated that the compounds those are dangerous with respect to human life, for the catalysts under investigation in the reaction of ammonia oxidation were not observed.

Thus, the 1 % $Pt/CeZrO_2$ and IC-42-1 catalysts can efficiently oxidize ammonia evolved in the course of carbamide decomposition to yield nitrogen oxides. The studies performed have demonstrated that the presence of CO_2 in the reaction mixture does not affect the ammonia oxidation process on these catalysts and does not result in the formation of toxic by-products in the reaction. The maximum yield of nitrogen oxides was about 85 % NO_x, but the catalyst containing 1 % $Pt/CeZrO_2$; efficiently operate at 500−600 °C, whereas the IC-42-1 catalyst gives a maximum yield of nitrogen oxides at a higher temperature (650−750 °C). Then, after cooling the gaseous mixture the nitrogen oxides can be absorbed with water to form nitric acid. Thus, the gaseous products of the ammonia oxidation represent molecular nitrogen and N_2O. The yield of the latter (unwanted) product decreases with increasing the reaction temperature for all the catalysts. In the future it is possible to modify of these catalysts, searching for the process conditions in order to increase the yield of nitrogen oxides for involving nitrogen into the intrasystem turnover.

CONCLUSION

After the wet combustion of organic wastes in the environment of H_2O_2 *via* the action alternating electric current and the subsequent decomposition of carbamide in the presence of urease, the gas phase contains mainly oxygen, nitrogen, carbon dioxide and ammonia. The ammonia evolved can be oxidized into nitrogen oxides within the temperature range of 500−600 °C on 1 % $Pt/CeZrO_2$ catalyst or within the range of 650−750 °C on IC-42-1iron oxide catalyst IC-42-1, with the further preparation of nitric acid salts those would be readily assimilated by plants. No compounds, whose presence in a LSS with humans is unacceptable (CO, H_2S, SO_2, mercaptans, cyanides, and isocyanates) were revealed in the gas phase. Small amounts of methane formed can be readily oxidized into CO_2, with the use of well-known catalysts.

Thus, *via* successive processing the components of the gas mixture produced in the course of the wet combustion, its composition could be presented by O_2, N_2 and CO_2 only. Because of this, the resulting gas mixture could be considered acceptable for using biological units of an LSS.

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