



HETEROGENEOUS-CATALYTIC REDOX REACTIONS IN NITRATE - FORMATE SYSTEMS

A.V. ANANIEV¹⁾, V.P. SHILOV¹⁾, I.G. TANANAEV¹⁾, Ph. BROSSARD²⁾, J.-Ch. BROUDIC²⁾.

¹⁾ – *Institute of Physical Chemistry RAS, 31, Leninsky prospect, 117951 Moscow, Russia.*

²⁾ – *CEA/VALRH/Marcoule, B.P.171, 30207 Bagnols/Seze, France.*

It was found that an intensive destruction of various organic and mineral substances - usual components of aqueous waste solutions (oxalic acid, complexones, urea, hydrazine, ammonium nitrate, etc.) takes place under the conditions of catalytic denitration. Kinetics and mechanisms of urea and ammonium nitrate decomposition in the system HNO_3 - HCOOH - Pt/SiO_2 are comprehensively investigated.

The behaviour of uranium, neptunium and plutonium under the conditions of catalytic denitration is studied. It is shown, that under the certain conditions the formic acid is an effective reducer of the uranium (VI), neptunium (VI, V) and plutonium (VI, IV) ions. Kinetics of heterogeneous-catalytic red-ox reactions of uranium (VI), neptunium (VI, V) and plutonium (VI, IV) with formic acid are investigated. The mechanisms of the appropriate reactions are evaluated.

Introduction

Formic acid is a very promising reagent for the application in the technologies involving into the nuclear fuel cycle. It can be successfully used for the displacing re-extraction of plutonium(IV) in the PUREX process [1] and for the isolation of plutonium(III) in the form of a hardly soluble formate [2]. The reducing property of the formic acid is used in the denitration reaction which is widely applied in the processes directed to a decrease of the nitrates content in the technological streams [3]. Recently we have found that in the presence of platinum catalysts the interaction between HNO_3 and HCOOH starts without any induction period which is typical for the reactions of auto-catalytic nature [4]. It was shown that application of catalysts allows to improve the denitration process from the point of view of safety and simplicity of operations. So far as the denitration processes are used mainly in the nuclear fuel cycle, the behaviour of different components of the waste solutions under the conditions of catalytic denitration is of certain scientific and practical interest. The present paper is concerned to the results of the original studies of the decomposition reactions of some organic and inorganic compounds – usual components of the radioactive waste solutions and, red-ox reactions of actinides in the system HNO_3 - HCOOH - Pt/SiO_2 .

The catalysts choice and preparation.

The particular features of radiochemical technology - aggressive nitric acid media, intensive radiation fields, put forward the rigid requirements to a choice of catalysts: high chemical and radiating stability of materials of the catalyst and support, mechanical durability, catalytic activity and simplicity of preparation. The platinum coated silica-gel (Pt/SiO_2) was chosen for the present study by the combination of properties.

Preparation of catalysts. A portion of 0.5-1.0 mm grain-size SiO_2 (KSK grade) is washed in the column with hot 3M HNO_3 until the effluent was free of Fe^{3+} as checked with NH_4SCN , then with water, and dried at 120°C during 24h. A computed volume of H_2PtCl_6 solution is added to a weighed portion of SiO_2 (~1.2 ml liquid per 1 g support). The mixture is carefully stirred and dried at 120°C. The Pt is reduced to the metal with hydrazine hydrate. The catalyst is poured into the boiling solution of reducer (1-2M) under stirring. The mixture is left for 30 min to complete the reduction; then the catalyst is separated on a glass filter, washed with hot 3M HNO_3 , water and finally dried at 100°C during 24h. The used catalyst was washed with hot 3M HNO_3 , water, dried at 100°C during 24h and utilised repeatedly.

The major amount of studies on catalysis in water solutions is carried out with application of Pt/SiO_2 . Despite of chemical stability in the nitric acid media and sufficient catalytic activity, this catalyst is not free from drawbacks connected to low mechanical durability of the support material and high cost of an active component - of platinum. Therefore, the further search of alternative materials of the catalyst and support is the important task from the practical and economic points of view.

Catalytic decomposition of organic and inorganic impurities – components of liquid radioactive waste.

The final processing of the radioactive waste is often difficult without preliminary removal of some undesirable admixtures like hydrazine, urea, oxalic acid, complexones, ammonium nitrate etc., which are usually present in the aqueous waste streams. In some cases [5,6], the task of the impurities decomposition in the nitric acid solutions may be resolved with the application of solid state catalysts. We have found that in nitrate solutions in the presence of formic acid, i.e. under the conditions of catalytic denitration process, the destruction of the mentioned above compounds proceeds more intensively. In some cases the catalytic decomposition becomes possible only in the presence of HCOOH (Table 1).

Table 1. Effect of HCOOH on decomposition of some compounds in the nitric acid solution in the presence of catalyst 1% Pt/SiO₂ (S/L = 0.1 g/ml).

Compound	[HNO ₃] ₀ , M	[HCOOH] ₀ , M	t, °C	τ _{1/2} , min
0.3M H ₂ C ₂ O ₄	2.5	0	60	4.5
0.3M H ₂ C ₂ O ₄	2.5	1.0	60	< 3
0.05M DTPA	2.0	0	60	12.4
0.05M DTPA	2.0	1.0	60	6.5
0.05M EDTA	2.0	0	-	No data
0.05M EDTA	2.0	1.0	60	4.5
0.2M N ₂ H ₄	2.0	0	50	33
0.2M N ₂ H ₄	2.0	1.0	50	26
0.1M (NH ₂) ₂ CO	2.5	0	60	No reaction
0.1M (NH ₂) ₂ CO	2.5	1.0	60	9
0.83M NH ₄ NO ₃	4.0	0	80	No reaction
0.83M NH ₄ NO ₃	4.0	~0.8*	80	~60

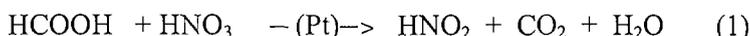
* the steady state concentration of HCOOH, which is continuously feed into the reactor.

The increase of the decomposition rate is obviously stipulated by the nitrous acid formation under the conditions of catalytic denitration. The decomposition of urea and ammonium nitrate in the system HNO₃ - HCOOH - Pt/SiO₂ was studied in detail to understand better the role of HNO₂ in the red-ox catalytic processes in nitric acid solutions.

Carbamide (urea) is used as a nitrous acid trap, particularly to cut out the pathway of nitration involving nitrosation, usually in concentrated nitric acid solutions [7]. In the radiochemical technology urea was applied as a anti-nitrous agent for the electrochemical processes of the uranium(VI) reduction [8] and silver recuperation from the nitric acid solution [9]. The final treatment of industrial and, particularly radioactive waste solutions often requires preliminary removal of urea as an undesirable admixture. Recently we have shown that the reaction of the heterogeneous catalytic denitration with formic acid proceeds successfully in the presence of urea and is accompanied by the decomposition of the latest [4].

Kinetics of (NH₂)₂CO catalytic decomposition was investigated. The analysis of gases generated during the reaction of the urea catalytic decomposition has been carried out on line by means of IR-spectroscopy and mass-spectroscopy methods. Preliminary experimental runs showed that in the absence of formic acid the catalytic decomposition of urea does not proceed at 60-90°C in the 0 - 8M HNO₃ solutions. At the same time, adding 0.1 - 2M HCOOH to 2M HNO₃ solution containing urea at 50°C causes, in the presence of 0.02 - 0.2 g/ml 1%Pt/SiO₂, the decomposition of (NH₂)₂CO accompanied by the denitration reaction. Kinetic measurements were carried out under the following conditions: [HNO₃]₀ = 0.7 - 7.0 M; [HCOOH]₀ = 0.2 - 1.3 M; [(NH₂)₂CO]₀ = 0.2 M; T = 50 - 80°C ; solid-to-liquid ratio S/L= 0.02 - 0.1 g/ml. All experiments were carried out in the presence of the catalyst 1%Pt/SiO₂. The reaction of (NH₂)₂CO decomposition in the presence of 0.2 - 1.3 M HCOOH and S/L= 0.02 - 0.1 g/ml starts at 60°C when the nitric acid concentration is equal or exceeds 2.0 M. In the range [HNO₃]₀ = 2 - 2.5 M the reaction is accompanied by the induction period followed by the fast decomposition of urea. At the higher nitric acid concentrations the reaction of urea decomposition starts leaving any induction time and proceeds by the "zero" order with respect to [(NH₂)₂CO]. The principal gaseous products accompanying the process were found to be CO₂, N₂O and N₂. Formation of the small amounts of NO₂ and traces of H₂ have been also revealed.

Consideration of kinetic regularities of the urea catalytic decomposition ("zero" order with respect to [(NH₂)₂CO]; presence of the induction time at small acidity) allows to conclude that the main process, responsible for the urea degradation is an interaction of (NH₂)₂CO with nitrous acid, catalytically generated in the reaction system as it take place in the process of catalytic denitration [4]. The reaction of the nitrous acid generation (the rate determining step) can be written then as



The change of the HNO_2 concentration in the process of urea decomposition is shown on Fig.1. $[\text{HNO}_2]$

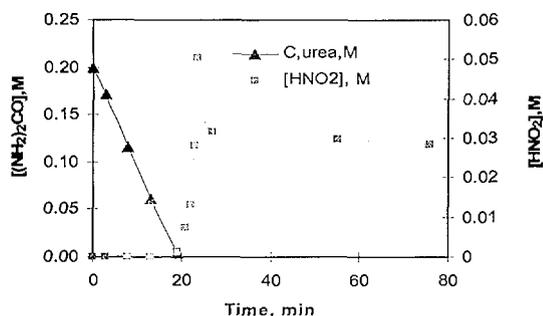
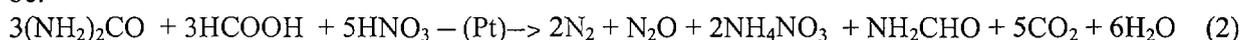


Fig.1. The nitrous acid accumulation in the process of the urea catalytic decomposition at $[\text{HNO}_3] = 3.3\text{M}$; $[(\text{NH}_2)_2\text{CO}]_0 = 0.2\text{M}$; $[\text{HCOOH}]_0 = 1.0\text{M}$; $t = 70^\circ\text{C}$; $\text{S/L} = 0.1 \text{ g/ml}$.

increases here from 0 to $1.26 \cdot 10^{-3} \text{ M}$ when $[(\text{NH}_2)_2\text{CO}]$ decreases from 0.2 to 0.005 M under the actual experimental conditions. Every moment nitrous acid exists in the solution in some steady-state concentration that is determined by the current urea concentration, the acidity, the temperature and the catalyst amount. After the complete urea decomposition the nitrous acid concentration increases sharply up to $\sim 0.06 \text{ M}$ then decreases down to $\sim 0.03 \text{ M}$ and remains almost constant up to the end of the catalytic denitration process.

The total stoichiometric reaction equation of the urea catalytic decomposition was found to

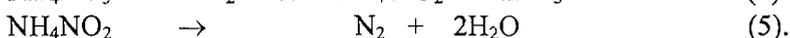
be:



It was shown that the products of the urea decomposition – formamide and ammonium nitrate undergo further transformation under the conditions of catalytic denitration. Formamide disappears due to a shift to the right the acidic hydrolysis equilibrium along with the decrease of the formic acid concentration which consumption accelerates with the beginning of the denitration reaction:



The decomposition of the ammonium nitrate proceeds as a result of the following reactions :



Being one of the important by-products of the radiochemical technology the ammonium nitrate is presented in the radioactive waste of the nuclear reprocessing plants. Ammonium nitrate is related to the class of the potentially hazardous chemical compounds because of its capability to a detonation in the solid phase under the certain conditions [10]. Therefore, the uncontrolled accumulation of NH_4NO_3 in the waste is not admissible from the point of view technological safety of the nuclear fuel cycle. Several methods for the ammonium nitrate destruction on the base of the catalytic denitration process were proposed and tested. The conditions for the effective and complete decomposition of NH_4NO_3 in the nitric acid solutions are determined.

The actinides catalytic red-ox reactions in the system $\text{HNO}_3 - \text{HCOOH} - \text{Pt/SiO}_2$

The denitration processes are used mainly in the nuclear fuel cycle; therefore the behaviour of different radioactive components of solutions and, especially, actinide ions under the conditions of catalytic denitration is of certain scientific and practical interest. It was shown in the series of active denitration tests that the presence in the solution up to 0.75M U(VI) and 0.1M Pu(IV) does not prevent from the successful catalytic denitration process. Some overconsumption of formic acid takes place at the catalytic denitration of the plutonium solutions in comparison with the nonactive tests. This fact is a possible consequence of the catalytic side reaction of the plutonium(IV) reduction. In fact, spectral analysis of the final denitrated solutions with the excess of HCOOH showed that up to 40% of Pu presents in the trivalent oxidation state. The observed partial reduction of Pu(IV) to Pu(III) can be caused by the catalytic reduction of plutonium by formic acid. The back oxidation is stipulated obviously by the nitrous acid which is generated in the solution during denitration. Thus, during the catalytic denitration, Pu(III) presents in the solution in some steady state concentration which is determined by the current composition of the reaction mixture, solid-to-liquid ratio and the temperature.

Hexavalent uranium, neptunium and plutonium, pentavalent neptunium and tetravalent plutonium are quite stable in the formate solutions though their formal oxidation potentials are higher than the standard potential of the couple HCOOH/CO_2 . However, we have found, that in the presence of platinum catalysts and anti-nitrous agents formic acid can effectively reduce hexavalent uranium, neptunium and plutonium; pentavalent neptunium and tetravalent plutonium in the nitrate solutions. The studied catalytic red-ox reactions of the actinide ions with HCOOH in the nitrate solutions are listed in Table 2.

Table 2. Heterogeneous catalytic red-ox reactions of actinides in the system $\text{HNO}_3 - \text{HCOOH} - \text{Pt/SiO}_2$.

N ^o	Reaction	Conditions	Remarks
I	$\text{UO}_2(\text{NO}_3)_2 + \text{HCOOH} + 2\text{HNO}_3 = \text{U}(\text{NO}_3)_4 + \text{CO}_2 + 2\text{H}_2\text{O}$	0,75M U(VI); 0.75-2.0M HCOOH; 0.02-0.1M N_2H_5^+ or >1.5M $(\text{NH}_2)_2\text{CO}$; 1-4M HNO_3 ; $t = 28-65^\circ\text{C}$; 0.1g/ml 1% Pt/SiO ₂ , 1% Pt/Anionites	In the presence of urea the reduction is not complete.
II	$2\text{NpO}_2^{2+} + \text{HCOOH} = 2\text{NpO}_2^+ + \text{CO}_2 + 2\text{H}^+$	$(1.85-30) \cdot 10^{-3}$ M Np(VI); 0.2-1.5M HCOOH; 0.1- 0.5M $(\text{NH}_2)_2\text{CO}$; 0.1-1.9M HNO_3 ; $t = 30-60^\circ\text{C}$; 0.01-0.1g/ml 1% Pt/SiO ₂	Diffusion controlled process ($E^* = 18.7\text{kJ/mole}$)
III	$\text{PuO}_2^{2+} + \text{HCOOH} + 2\text{H}^+ = \text{Pu}^{4+} + \text{CO}_2 + 2\text{H}_2\text{O}$	$6.52 \cdot 10^{-3}$ M Pu(VI); 0.1-1.0M HCOOH; 0.1M $(\text{NH}_2)_2\text{CO}$; 0.6-1.9M HNO_3 ; $t = 20-50^\circ\text{C}$; 0.1g/ml 1% Pt/SiO ₂	Diffusion controlled process ($E^* \approx 19\text{kJ/mole}$)
IV	$2\text{NpO}_2^+ + \text{HCOOH} + 6\text{H}^+ = 2\text{Np}^{4+} + \text{CO}_2 + 4\text{H}_2\text{O}$	$(1.24-6.2) \cdot 10^{-3}$ M Np(V); 0.01-1.0M HCOOH; 0.1-0.5M $(\text{NH}_2)_2\text{CO}$; 0.2-1.8M HNO_3 ; $t = 40-70^\circ\text{C}$; 0.025-0.1g/ml 1% Pt/SiO ₂	
V	$2\text{Pu(IV)} + \text{HCOOH} = 2\text{Pu(III)} + \text{CO}_2 + 2\text{H}^+$	$1.2 \cdot 10^{-2}$ M Pu(IV); 0.2-0.7M HCOOH; 0.1-0.5M $(\text{NH}_2)_2\text{CO}$; 0.27-1.97M HNO_3 ; $t = 30-60^\circ\text{C}$; 0.01-0.1g/ml 1% Pt/SiO ₂	

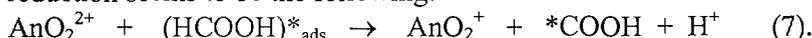
Kinetic data obtained for the reactions I-V allow revealing the following scheme of the heterogeneous catalytic interaction between actinide ions and HCOOH.

The most likely, all the reactions start with the activated adsorption of formic acid on the active centers of the catalyst:

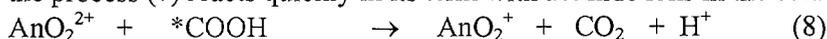


Formic acid, being a di-electron reducer reacts usually with oxidants through the stage of the formation of the *COOH radicals, possessing high reactivity [11].

Taking into account the written above, the path of the processes I-III of the actinide(VI) catalytic reduction seems to be the following:



The electron transfer between Np, Pu (VI) and $(\text{HCOOH})^*_{\text{ads}}$ proceeds very quickly and the rate of the whole reaction is determined by the diffusion processes ($E^* \sim 19 \text{ kJ/mole}$). In the case of U(VI) the reaction (7) is the rate determining ($E^* \sim 48 \text{ kJ/mole}$) process and it is accompanied possibly by the formation of the activated complex $\{\text{O}=\text{U}^{2+}=\text{O}---\text{H}-\text{COOH}\}^*_{\text{ads}}$ on the surface of the catalyst. The radical *COOH formed in the process (7) reacts quickly in its term with actinide ions in the solution:

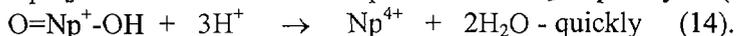
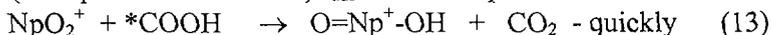
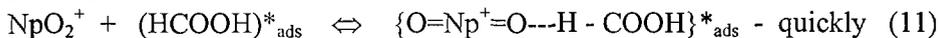


Pentavalent uranium and plutonium under the actual experimental conditions are not quite stable in the solution toward the reaction of disproportioning:

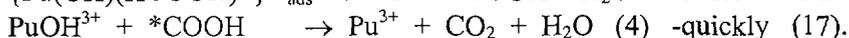
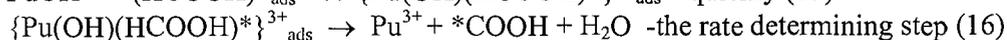


Processes (8,9) and (10) are not distinguishable by kinetic and stoichiometric means. Therefore it is not possible to give a preference to one or another way for the An(IV) formation by the reactions I and III.

The interaction between neptunium(V) and adsorbed HCOOH (reaction IV) proceeds by the scheme:



The mechanism of the of the plutonium(IV) catalytic reduction (reaction V) was found to be the following:



It should be noticed that the catalytic red-ox reactions of actinide ions with formic acid in the presence of urea as a nitrous acid trap proceed completely at the nitric acid concentration below 2M. The increase of $[\text{HNO}_3]$ over $\sim 2\text{M}$ leads to the catalytic decomposition of urea accompanying with an abundant formation of gases, followed by the denitration of the solution. Under these conditions, at first, actinide ions

are reduced in some extent ($\text{Np(V)} \rightarrow \text{Np(IV)}$; $\text{Pu(IV)} \rightarrow \text{Pu(III)}$) and then, they are oxidised back by HNO_2 when the catalytic decomposition of urea is completed. Reactions **II** and **III** proceed partially even in the absence of urea but their yield is determined by the equilibrium reactions of AnO_2^{2+} ions with nitrous acid [12,13]. The catalytic reaction **I** of uranium(VI) with formic acid in the nitrate solutions starts when the concentration of urea exceeds 1.3M. The reduction is slow and incomplete. Probably, the anti-nitrous "force" of carbamide is not enough to prevent the back oxidation of uranium(IV) by HNO_3 that is strongly catalyzed by traces of nitrous acid [8]. The uranium(IV) catalytic reduction with HCOOH proceeds better in the presence of small quantities of hydrazine as a nitrous acid trap. Under these conditions the reduction proceeds even faster than the catalytic reaction with hydrazine as a reducing agent.

The results of this work allow to conclude that the system $\text{HCOOH} - \text{HNO}_3 - \text{Pt/SiO}_2$ may be successfully applied for the stabilization of actinide ions in the low oxidation states under their mutual presence. This system may be possibly used for the separation of neptunium and plutonium during the waste reprocessing or for the isolation of ^{238}Pu from the irradiated ^{237}Np targets by the extraction method. The choice of the optimal conditions for the realization of the processes may be done on the base of the experimental data, obtained in this study.

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