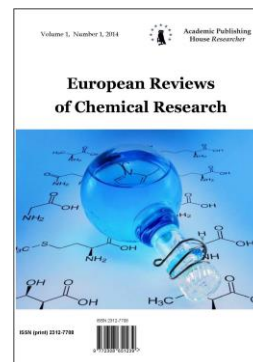


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Viscosity Properties of an Aqueous Suspension $\text{Pd}(\text{NO}_3)_2\text{-Al}_2\text{O}_3\text{-La}_2\text{O}_3\text{-HAc-H}_2\text{O}$ for Afterburning Catalysts

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Abstract

The boundary conditions of formation of hydroxides are determined by calculation of ion equilibrium with use of thermodynamic constants of metals For system " $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ ". Possibility of decrease in dynamic viscosity of the " $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ ", suspension having pH = 3 at addition of 1% of an aqueous solution is experimentally shown cation-active surfactant at 1.74 time: with 850.62 to 488.95 mPa·s. The morphology of particles of suspension before and after the addition in it surfactant cation-active Praestol 655 FC is investigated.

Keywords: afterburning catalysts, ion equilibrium, viscosity, palladium (II) nitrate, suspensions, ion equilibrium, surface-active substances, surfactant, lanthanum oxide.

Introduction

Combustion gases of cars are the main source of pollution of the air atmosphere of the cities. The exhaust gases of vehicles using gasoline, in contrast to vehicles that using on diesel fuel, contain lead compounds. At combustion of fuel in the car engine, products of combustion form the "specific poisonous cocktail" including products of imperfect combustion such as white damp, nitrous oxide, aldehydes, ketones, unsaturated hydrocarbons, and also peroxidates, dioxide of sulfur, compound of lead, soot and many other. Special catalysts of afterburning are used to cleaning and neutralization of combustion gases of petrol engines [1]. Currently, the biggest distribution among them was received by catalysts on the basis of compositions of the platinum metals deposited on porous oxide of aluminum [2, 3]. Palladium treat oxidizing catalyst, it promotes the oxidation of unburned hydrocarbons into water vapor, carbon monoxide into carbon dioxide. Due to its high catalytic ability are considered most effective. The oxides of rare earth elements included in composition of the catalyst interact with platinum metals, and prevent the sintering of the active component at the long-time heating.

The disadvantage of a palladium catalyst based on $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ system used for a complete series of a number of domestic cars is the complexity of its preparation.

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In the result of arising in disperse system the interaction of aluminum oxide phase, containing oxides of rare earth elements, with a solution of palladium salt there is an increase in viscosity of suspension. This complicates its putting of impregnating method on a ceramic block of afterburner catalyst, influences its oxygen capacity, reduces overall performance. The actual task optimizes the rheological properties of an aqueous suspension "Pd(NO₃)₂ – Al₂O₃ – La₂O₃ – HAc – H₂O", is used for the manufacture of catalysts for afterburning of exhaust gases.

For decrease in viscosity of suspensions usually use change of pH and temperature, ultrasonic processing, change of suspension preparation technology. One of the paths reducing viscosity of suspension is the additive in system of surface-active substances. The mechanism of surfactant action in this case is up to the end not clear, however the application results of different types surfactant for increase in oxygen capacity of afterburner catalyst are given in works [4, 5].

The aim of the present work was research of rheological properties of an aqueous suspension Pd(NO₃)₂ – Al₂O₃ – La₂O₃ – HAc – H₂O putting on the ceramic block of afterburner catalyst at addition in its surfactant, change of multiplicity of dilution and change pH.

Experimental part

The basic composition of an aqueous suspension for afterburner catalyst of exhaust gases was reasonable by the main requirements present to them in scientific and technical literature for ensuring effective work [1-9]. The oxidizing component for post-combustion exhaust gases has been selected palladium. The carrier of an oxidizing component used aluminum oxide (II) with the addition 4 % rare earth metal (lanthanum oxide (II)). As the reactionary environment for oxidation of some organic substances ethane acid (acetic acid) was used. Synthesis of suspension was carried out with a preliminary grinding of the powdery oxides of aluminum and lanthanum to the sizes in the limit 6.5-9.5 microns.

Experiments on measurement of dynamic viscosity of suspension were made by method of capillary viscosimetry, which is rely on Poiseuille's law, at 298 K. For this purpose in work Ostwald's viscometer and Brukfeld's viscometer were used.

For an estimate of the sizes and research of suspension particles morphology the analyzer of the sizes of particles of HORIBA LB-550 was used and the scanning electronic microscope in the scanning mode JEOL JXA-8500F (Japan) with the probe microanalyzer at the accelerating voltage of the electron beam tension from 10 to 30 kV was used.

Results and discussion

One of the main tasks, from the point of view of the organization of process, is the possibility of forecasting the boundary conditions for obtaining of possible connections. For optimization of suspension composition the areas concentration and pH formations of basic hydroxides of Pd(OH)₂, Al(OH)₃, La(OH)₃ metals in an system Pd(NO₃)₂ – Al(NO₃)₃ – La(NO₃)₃ – HAc – H₂O by the technique described in [10, 11] calculation thermodynamic was carried out.

For this purpose, the analysis of the ionic balance by a technique [12] which are established in the investigated multicomponent system was carried out. At calculation of formation in solution of known multinuclear complexes of Me_p(OH)_n metals was also took into account.

In the first approximation, the formation boundary conditions in system the phases hydroxides Pd(OH)₂, Al(OH)₃, La(OH) meet equality of ionic product IP_{Me(OH)_n} to solubility product of the meet hydroxide of metal SP_{Me(OH)_n}, being at this temperature a constant (1):

$$IP_{Me(OH)_n} = SP_{Me(OH)_n} \quad (1)$$

For begin of solid phase formation process the equality has to be carried out

$$SP_{Me(OH)_n} = [Me^{n+}]_H [OH^-]_H^n = (\alpha_{Men+} \cdot C_i) \cdot [OH^-]^n, \quad (2)$$

where α_{Men+} is the a share of the metal uncomplexed ions capable to enter chemical reaction, and C_i is the initial concentration of salt of metal in solution.

According to [11] design formula allowing to calculate value of minimum necessary concentration of salt of metal in a logarithmic form has an appearance (3):

$$pC_i = pSP_{Me(OH)_n} - p\alpha_{Men+} - npK_{H_2O} + npH^+, \quad (3)$$

where K_{H_2O} is the a water ionization constant.

The equation (3) enough fully describes difficult heterogeneous process of metal hydroxide formation. Definition pC_i was carried out with use of thermodynamic constants (K_{H_2O} , $SP_{Me(OH)_n}$) [13-15].

Results of calculation at a temperature of 298 K in coordinates $pC_i = f(pH)$ are presented graphically in Fig. 1. The obtained data were used for a select pH suspensions from the viewpoint of completeness of sedimentation and stability of palladium s, aluminum and lanthanum hydroxide. Optimum pH should be considered higher than 5.0.

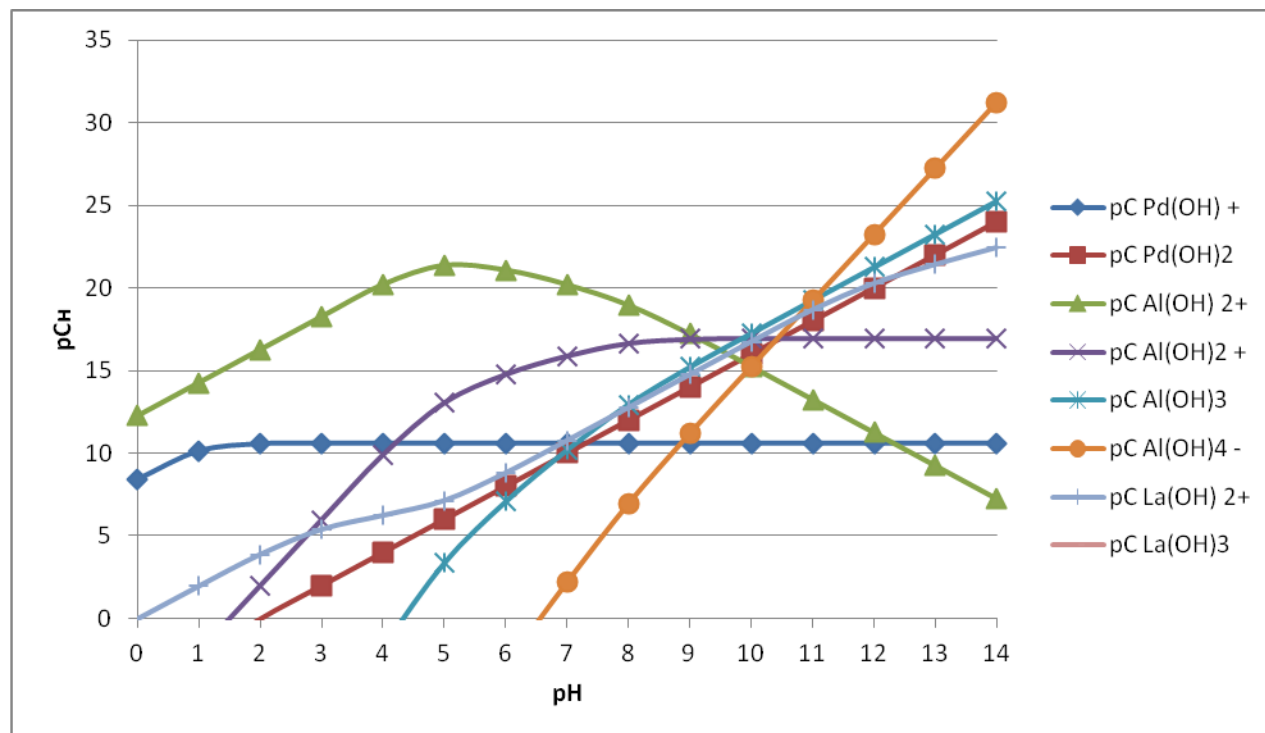


Fig. 1. The boundary conditions the formation of metal hydroxides and hydroxy complexes of palladium, aluminum, lanthanum, in the " $Pd(NO_3)_2 - Al(NO_3)_3 - La(NO_3)_3 - HAc - H_2O$ " at 298 K

Disperse hydroxide systems are structured and for an explanation of the mechanism of their formation it is possible to use some consistent patterns inherent in hallogenidny systems, established in work [16, 17]. As representations of authors in "reactionary mixes with their inherent high saturation on the besieged solid phase at the expense of the cooperative and fluctuation phenomena the molecular complexes, associates, clusters, submicronic formation, having the colloidal nature or being products of structuring colloidal particles can be formed". The presence of charged groups in the molecules causes special hydrodynamic characteristics of polyampholytes solutions. Their behavior substantially depends on the value pH and the ionic force of the environment. By increasing in pH of the environment viscosity of suspension, as a rule, increases as associates increase in volume owing to straightening of formation polymeric.

Analysis of the literature [18-21] showed that the behavior and properties of viscous fluids is significantly affected by their composition, including existence of surface-active substances of various type.

The results of the particles sizes measurement in suspension and an assessment of their quantitative distribution showed that addition in suspension of 1 % of water solution Praestol 655 FC surfactant in the ratio 1:10 sharply reduces dispersion of particles by the sizes, at the same time increasing variations of the particles average size (Fig. 2).

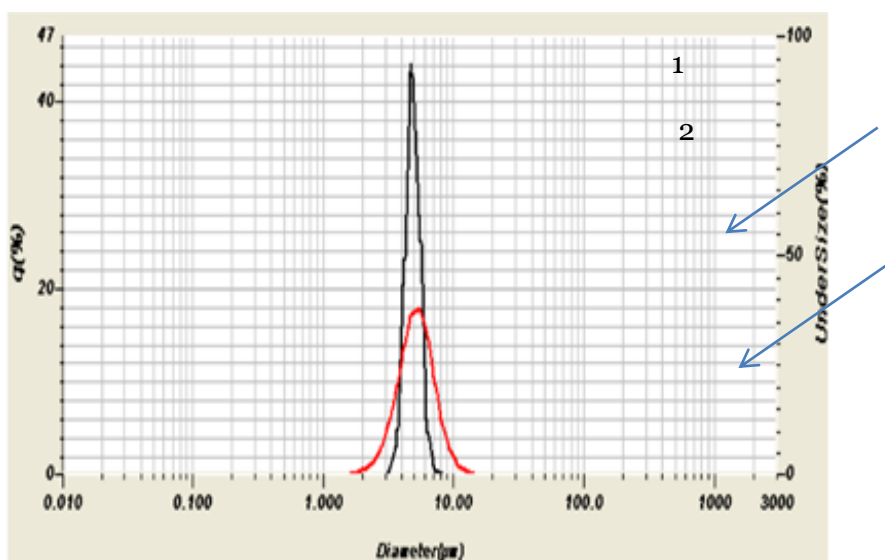


Fig. 2. Comparative characteristics of particles distribution by the suspension sizes $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ at its dilution by 1:10 water (1) and 1 % water solution Praestol 655 FC (2) surfactant at pH = 3

The particles microimages of the studied suspension to absence surfactant and after its introduction in the form of 1 % of water solution are presented for comparison in Fig. 3.

It is clearly visible that the suspension containing surfactant has considerably the smaller average particles size that probably is connected with its adsorption action which is slowing down integration of particles.

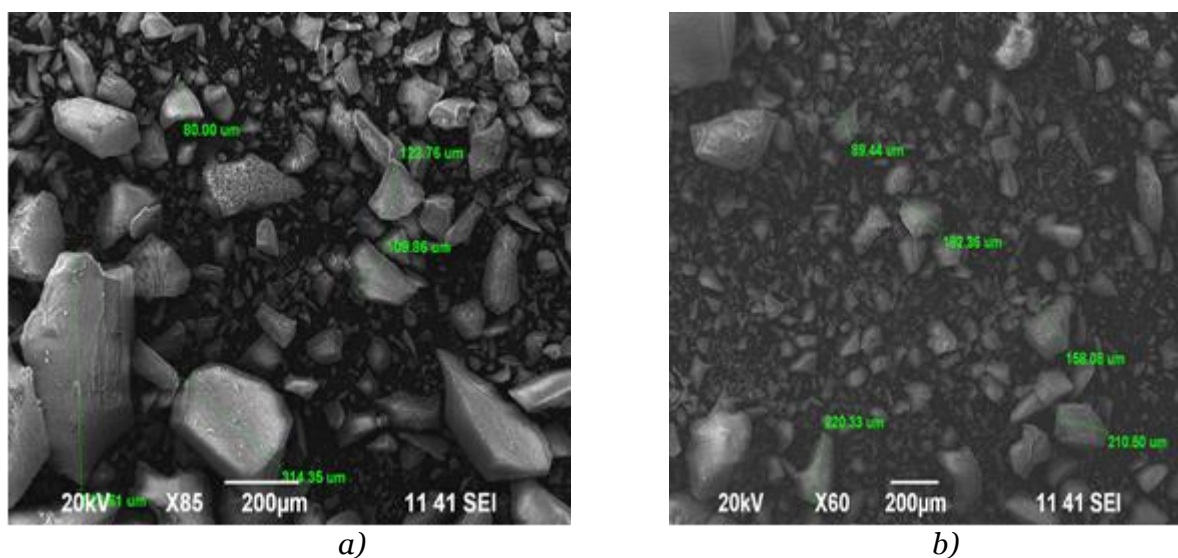


Fig. 3. Electronic and microscopic images of the suspension particles $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ to (a) and after an additive in it 1% of water solution Praestol 655 FC surfactant in the ratio 1:10 (b)

In the real work influence on properties of suspension viscous an additive perspective cation-active Praestol 655 FC surfactant was investigated. For comparison purposes efficiency of addition surfactant in system dependence of change of dynamic viscosity of suspension on dilution by its water was also received. Below in fig. 4 the results of dilution influence on dynamic suspension viscosity of dilution by water (1) and one-percentage water solution surfactant (2) are given below.

As appears from Fig. 4 the increase dilution frequency rate of 1 % water solution Praestol 655 FC surfactant to level 1.12 leads to bigger decrease in dynamic viscosity of suspension, than dilution

by its water. The same time the maximum distinctions in viscosity reaching 1.74 times are observed at frequency rate of dilution 1.10. At the dilution more than 1.12 situation changes on the return and dilution by water becomes more preferable. When putting suspension on the ceramic block strong dilution is undesirable as reduces the oxygen capacity of the catalyst. Therefore, the recommended dilution level providing considerable advantage of 1 % of water solution Praestol 655 FC surfactant should be considered dilution level 1.10.

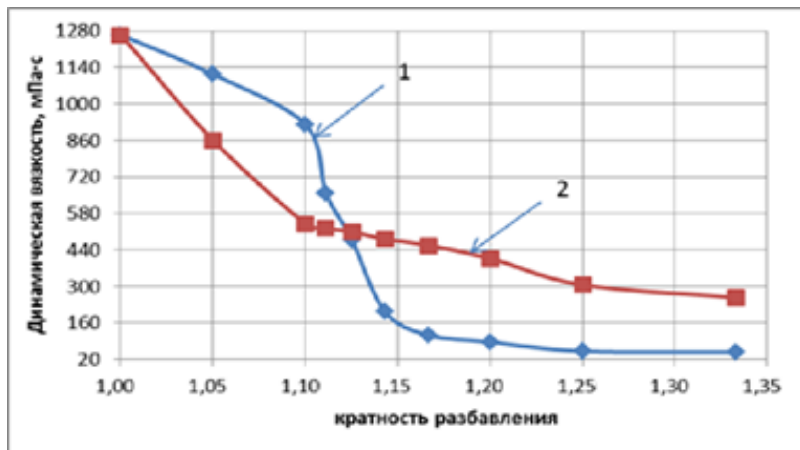


Fig. 4. The change of dynamic viscosity of suspension $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ at a temperature of 298 To from frequency rate of its dilution by water (1) and 1 % water solution Praestol 655 FC (2) surfactant

The dependence of the dynamic viscosity of the studied suspension at various pH values ranging from 3 to 5 in cases of dilution it 1 % aqueous surfactant Praestol 655 BC (2) at 1.10 multiplicity of dilution shows on Fig. 5.

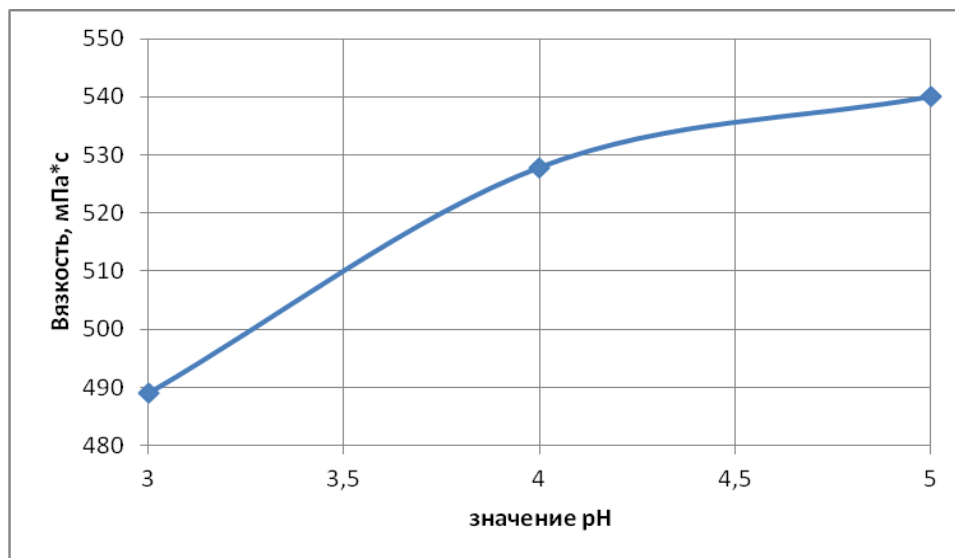


Fig. 5. Change of dynamic viscosity of suspension $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ at a temperature of 298 To from value pH at frequency rate of its dilution by 1.10 water (1) and 1 % water solution Praestol 655 FC (2) surfactant

Dependencies in fig. 5 show a decrease in the viscosity of the suspension from 540.06 to 488.95 MPa c for an acidic working environment (pH = 3). Increasing in dynamic viscosity of suspension with pH increases is connected with the formation of particles, more resistant to destruction.

Conclusion

By calculation of ionic balances in the "nitrate of palladium (II)-oxide of aluminum (II)-oxide of lanthanum (II)" system boundary conditions and the concentration fields of education of hydroxides of metals are defined.

In the course of experimental studies found that suspension $\text{Pd}(\text{NO}_3)_2 - \text{Al}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{HAc} - \text{H}_2\text{O}$ dilution of 1 % water solution cation-active Praestol 655 FC surfactant in the ratio 1:10 reduces its dynamic viscosity 1.74 times stronger in comparison with similar dilution by water.

It is shown that the most preferable range for receiving this suspension is the sour pH area.

By electronic and microscopic researches and measurements of the sizes of suspension particles it is revealed that dilution of its 1 % water solution Praestol 655 FC surfactant reduces the average size of particles and their dispersion by the sizes.

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