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MECHANISMS
OF CATALYTIC REACTIONS

Kinetic Studies on the Hydrogenation of Nitrate in Water Using Rh/Al_2O_3 and $Rh–Cu/Al_2O_3$ Catalysts[1]

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Abstract—Liquid-phase reduction NO_3^- using monometallic and bimetallic catalysts (5% Rh/Al_2O_3, 5% Rh – 0.5% Cu/Al_2O_3, 5% Rh–1.5% Cu/Al_2O_3, 5% Rh–5% Cu/Al_2O_3 and a physical mixture of 5% Rh/Al_2O_3 and 1.5% Cu/Al_2O_3) was studied in a slurry reactor operating at atmospheric pressure. Kinetic measurements were performed for a low concentration of nitrate (0.4×10^{-3}–3.2×10^{-3} mol dm^{-3}) and the temperature range 293–313 K. From the experimental data, it was found that the reduction of nitrate is first order with respect to nitrate. On the basis of the rate constants, the apparent activation energy was established using a graphic method.

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INTRODUCTION

With increasing population and intensive development of harmful policy, the amount of waste-polluted waters is growing. The contamination particularly poses a danger to plankton living in seas and oceans, which provides Earth's ecosystem with 50% of its oxygen and 30 billion tons of organic substances. Water contamination can be of chemical, physical, physiological, and biological nature.

Physical contamination of water refers to changes in color, clarity, and temperature. Physiological contamination is responsible for nasty taste and smell usually caused by chemicals such as mercaptanes, amines, sulfides, and phenol. Biological contamination is caused by bacteria, viruses, and protozoans. This type of contamination is responsible for certain diseases.

Chemical contamination is common and can be of different types. Compounds resistant to biological decomposition are particularly harmful because they remain present in water for a long time. These are detergents, pesticides, and heavy metals. Nitrates and precursors of carcinogenic nitrosoamines [1], as well as compounds leading to eutrophication of lakes, are also dangerous.

Due to the fact that nitrates are harmful to human health, certain steps have been taken. The World Health Organization (WHO) set a limit of NO_3^- ion content in drinking water at 50 mg NO_3^-/dm^3. The same level of nitrate concentration in consumer water is recommended by Polish and European norms. Therefore, producers of consumer waters are obliged to remove excessive amounts of NO_3^- ions from water.

Nitrates can be removed with the use of the selective ion exchange method and biological methods. Those methods, however, have many drawbacks mainly connected with environmental protection. One of the alternative methods of nitrate removal from water is their catalytic transformation into harmless nitrogen (N_2) [2, 3]. However, studies of catalytic reduction of nitrates on metallic catalysts prove the formation of ammonia as a by-product, which is also dangerous. The catalytic hydrogenation of NO_3^- in water involved the use of noble metal catalysts [4–22]. Among these metals only palladium catalysts have been studied widely in this reaction. Rhodium catalysts are known as good catalysts in reduction processes, too. In the face of these facts, it is justifiable to carry out studies aimed at designing catalytic systems of high selectivity to N_2.

The activity and selectivity can be improved by the addition of a second metal from groups 11, 12, 13, and 14. Usually, copper, tin, indium, or zinc was used as a promoting second metal [4–22]. Although many papers connected with studies of activity and selectivity towards nitrogen formation have been published, the changes in the catalytic behavior as a function of the second metal are still not fully understood and a general reaction mechanism has not yet been proposed. To establish a mechanism of a given reaction, kinetic studies are necessary.

This paper describes kinetic studies on the hydrogenation of nitrate in water at 293–313 K using Rh and Rh–Cu on alumina catalysts. We estimated the order of the reaction in relation to nitrate(V), which was hydrogenated using hydrogen in abundance. The hydrogen

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[1] This article was submitted by the authors in English.

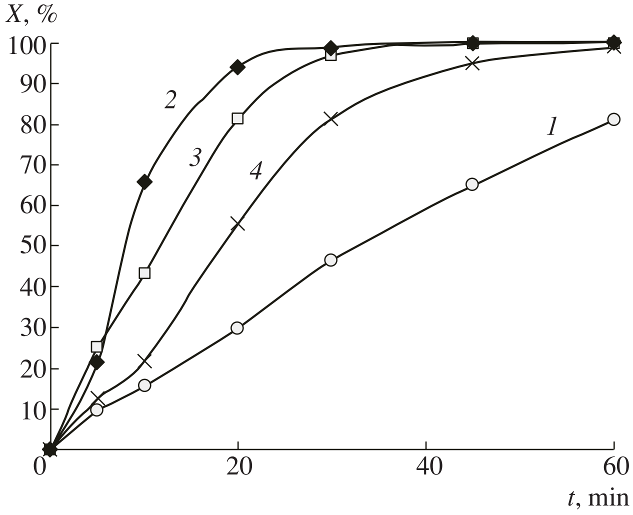


Fig. 1. Conversion of nitrates in the presence of the catalysts (*1*) 5% Rh/Al_2O_3, (*2*) 5%Rh–0.5% Cu/Al_2O_3, (*3*) 5% Rh–1.5% Cu/Al_2O_3, and (*4*) 5% Rh–5% Cu/Al_2O_3 as a function of time. Reaction conditions: catalyst weight 1 g, temperature 293 K, reactant $C_{NO_3^-} = 1.6 \times 10^{-3}$ mol dm^{-3}, H_2 (1 atm, 0.2 dm^3/min).

flow was constant (0.2 dm^3/min) during the reaction. From our results, we also calculated a rate constant for the temperatures 293, 298, 303, 308, and 313 K and the activation energy.

EXPERIMENTAL

Catalyst Preparation

Catalysts 5% Rh/Al_2O_3 and 1.5% Cu/Al_2O_3 (Al_2O_3, Cabot, $S_{BET} = 111$ m^2/g) were prepared from water solutions of $Rh(NO_3)_3$ (a.q., National Mint of Poland) and $Cu(NO_3)_2 \cdot 3H_2O$ (a.q., POCh Gliwice, S.A.) by aqueous impregnation. A bimetallic catalyst 5% Rh–1.5% Cu/Al_2O_3 was prepared from water solutions of both salts by coimpregnation. The water was evaporated at an increased temperature (353 K) under vacuum. The catalysts were dried in air at 383 K for 6 h, calcined at 773 K for 4 h in air atmosphere, and then reduced in hydrogen atmosphere for 2 h at 573 K.

Catalytic Measurements

The hydrogenation of the nitrate solution ($[NaNO_3]_0 = 0.4 \times 10^{-3}$; 0.8×10^{-3}; 1.6×10^{-3}; 3.2×10^{-3} mol dm^{-3} ($NaNO_3$, a.q., POCh Gliwice, S.A.)) was performed in a thermostated glass reactor equipped with a stirrer, a hydrogen supply system, a burette, and a pH electrode. The ammonia formed during the reduction of nitrate was neutralized by the addition of an aqueous solution of HCl (5×10^{-2} mol dm^{-3}) to maintain constant pH 5.5 in the reaction medium. The reaction was conducted at 293–313 K. The mixture was stirred at 1300 rpm, and hydrogen was bubbled through at 0.2 dm^3/min. No temperature rise due to the heat of the reaction was observed in any of the runs since the reactor was operated with low nitrate concentrations (0.4×10^{-3}–3.2×10^{-3} mol dm^{-3}). No pressure control was required since the total operating pressure in the system was equal to atmospheric pressure. As three phases were present in the reactor, the used system is treated as a slurry reactor.

The concentrations of NO_3^- and NO_2^- ions in the reaction mixture were measured with HPLC. Samples of the reaction medium were taken, filtered, and analyzed using a liquid chromatograph LaChrom (Merck Hitachi) coupled with a variable wavelength UV detector LaChrom L-7400 (Merck Hitachi). The analytical wavelength was 210 nm. In our investigation, a Merck C_{18} LiChrospher RP-18 (5 μm) column (250 × 4.0 mm I.D.) was used. The water solution of octyloamine phosphorate (5×10^{-3} mol dm^{-3}, pH 6.3) was used as a mobile phase. The flow rate of octylamine phosphorate was 1 cm^3/min.

For the liquid samples, the concentrations of NH_4^+ ions were analyzed spectrophotometrically with the use of Amonia-Test (2.6–193 mg NH_4^+/dm^3, Merck).

RESULTS AND DISCUSSION

The results of the reduction of nitrates are expressed as conversion (*X*, %) and selectivities (*S*, %). Those parameters were defined as

$$X = \left[\frac{C_0 - C}{C_0}\right] \times 100\%,$$

$$S_{NH_4^+} = \left[\frac{C_{NH_4^+}}{C_0 - C}\right] \times 100\%,$$

$$S_{NO_2^-} = \left[\frac{C_{NO_2^-}}{C_0 - C}\right] \times 100\%,$$

$$S_{N_2} = 100\% - S_{NH_4^+} - S_{NO_2^-},$$

where $S_{NH_4^+}$, $S_{NO_2^-}$, and S_{N_2} are selectivity towards ammonia, nitrites, and nitrogen, respectively; C_0 is the molar concentration of nitrates at the beginning of the reduction; C is the molar concentration of nitrates after time t; $C_{NH_4^+}$ is the molar concentration of ammonia after time t; and $C_{NO_2^-}$ is the molar concentration of nitrites after time t.

Figure 1 presents changes in the conversion of nitrates for a monometallic system (5% Rh/Al_2O_3) and for rhodium catalysts supported on Al_2O_3 and modified with copper. The supported monometallic rhodium cat-

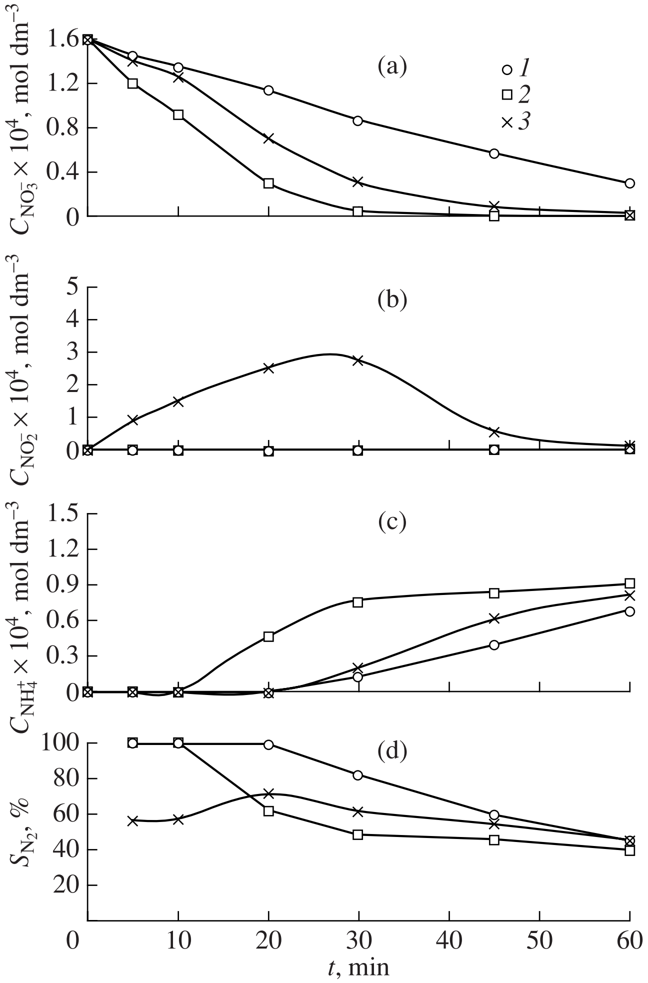


Fig. 2. The concentration profiles as a function of time for the reduction of 1.6×10^{-3} mol dm^{-3} nitrate solution at 293 K over Rh–Cu/Al_2O_3 catalysts ((*1*) 5% Rh/Al_2O_3, (*2*) 5% Rh–1.5% Cu/Al_2O_3, and (*3*) 5% Rh–5% Cu/Al_2O_3). (a) The concentration profiles of nitrates as a function of time; (b) The concentration profiles of nitrites as a function of time; (c) The concentration profiles of ammonia as a function of time; (d) The selectivity towards N_2.

alyst is active in the reduction of nitrates. The value of conversion of nitrates over 5% Rh/Al_2O_3 is considerably higher than in the case of monometallic palladium catalysts [23, 24]. The conversion obtained for bimetallic Rh–Cu/Al_2O_3 catalysts is not much higher than in the case of the monometallic system.

The reduction of nitrates via nitrites to nitrogen and ammonia over Rh–Cu/Al_2O_3 and Rh/Al_2O_3 catalysts is presented in Figs. 2a–2d.

The results in Fig. 2a show that the addition of copper to the rhodium catalyst decreases the time that is necessary for a complete reduction of nitrates. However, the activity for the monometallic catalyst at the end of the run is also high.

The release of nitrites into the solution during the reduction of nitrate was higher for catalysts with higher Cu contents (Fig. 2b). For catalysts with a small amount of copper, the presence of nitrites was not observed in the reaction solution.

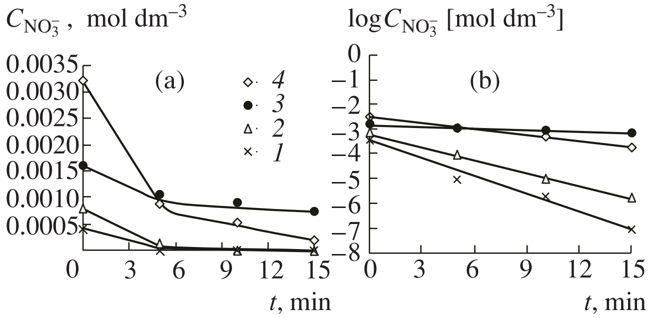


Fig. 3. The concentration of NO_3^- and logarithm of NO_3^- concentration as a function of the time of hydrogenation of nitrate over 5% Rh–1.5% Cu/Al_2O_3 at 293 K. Initial concentrations of NO_3^- are as follows: (*1*) 0.4×10^{-3} mol dm^{-3}; (*2*) 0.8×10^{-3} mol dm^{-3}; (*3*) 1.6×10^{-3} mol dm^{-3}; (*4*) 3.2×10^{-3} mol dm^{-3}.

The catalytic reduction of nitrates requires the formation of sufficient mono- and bimetallic sites on the surface of bimetallic catalysts. With a greater content of copper in Rh–Cu/Al_2O_3 catalysts, the chance of forming bimetallic sites increases. Because those bimetallic sites are active for nitrate reduction to nitrite in the case of 5% Rh–5% Cu/Al_2O_3, more intermediate nitrites were released into the reaction solution (Fig. 2b).

The formation of ammonia was low at the beginning of the reaction over all catalysts (Fig. 2c). The lowest amount of ammonia formation during the degradation of nitrates was for the 5% Rh/Al_2O_3 catalyst. The addition of copper to monometallic rhodium catalysts increased the concentration of ammonia in the reaction mixture.

Figure 2d shows the selectivity towards N_2 in the reduction of nitrates obtained for a monometallic system (5% Rh/Al_2O_3) and for rhodium catalysts supported on Al_2O_3 and modified with copper. These results of our investigations confirm the high selectivity of monometallic rhodium catalysts. Unfortunately, the addition of copper to rhodium catalysts does not increase the selectivity to N_2.

Figure 3b shows the logarithm of nitrate concentration as a function of different initial nitrate ion concentrations for 5% Rh–1.5% Cu/Al_2O_3. Those relationships are linear for all initial concentrations of NO_3^- in the first 15 min of the reaction. From this study we calculate the rates of reaction. The logarithmic relationship between the reaction rates for the hydrogenation of NO_3^- and the concentrations of NO_3^- (0.4×10^{-3}–3.2×10^{-3} mol dm^{-3}) is shown in Fig. 4.

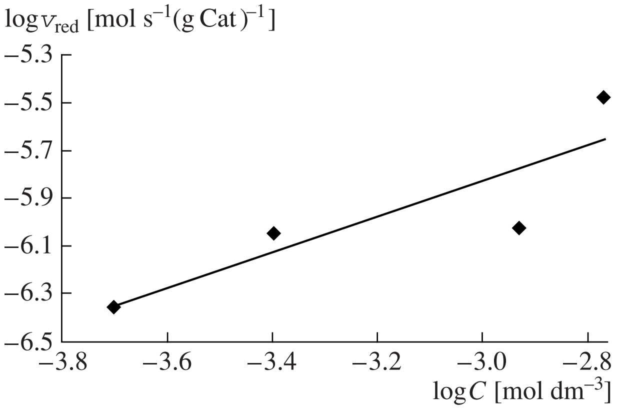


Fig. 4. Dependences of the reaction rates on concentrations of NO_3^- in the hydrogenation of NO_3^- over 5% Rh–1.5% Cu/Al_2O_3. Reaction conditions: catalyst weight 1 g, temperature 293 K, reactant NO_3^- (0.4×10^{-3}–3.2×10^{-3} mol dm^{-3}), H_2 (1 atm, 0.2 dm^3/min). The rates of the reaction (v_r) were calculated for the first 15 min of NO_3^- reduction as the number of moles of NO_3^- converted to products [mol s^{-1} (g Cat)$^{-1}$].

From the slopes of the plots, the reaction order of NO_3^- hydrogenation was determined to be 0.7 with respect to the NO_3^- concentration.

The degradation of nitrates was also measured at different temperatures (293–313 K) over 5% Rh–1.5% Cu/Al_2O_3 to define other kinetic parameters. For the experimental data and on the basis of the fact that the depletion of nitrate follows approximately a first order decay, the values of rate constants were calculated ($k = 2.1 \times 10^{-3}$ at 293 K, $k = 2.7 \times 10^{-3}$ at 298 K, $k = 4.0 \times 10^{-3}$ at 303 K, $k = 4.4 \times 10^{-3}$ at 308 K, $k = 4.6 \times 10^{-3}$ at 313 K). From the slopes of the straight line in Fig. 5. the apparent activation energy was found to be 31 kJ/mol in the process of the liquid-phase reduction of aqueous nitrate over the Rh–Cu bimetallic catalyst.

Apparent activation energies for the monometallic rhodium catalyst and for the physical mixture of 5% Rh/Al_2O_3 and 1.5% Cu/Al_2O_3 catalysts were estimated in the same way and are summarized in the table.

A large number of studies of nitrate hydrogenation on the effects of an additive metal and support have been reported [1–20], while only a few have been published on the kinetics and mechanism [10–12, 21, 22].

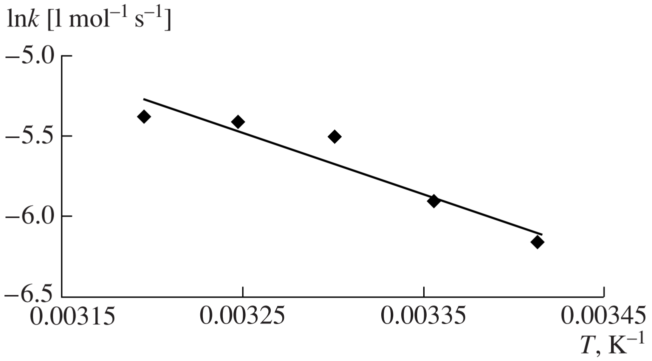


Fig. 5. Arrhenius plot for the reduction of nitrates on the 5% Rh–1.5% Cu/Al_2O_3 catalyst. Initial concentration of NO_3^- is 1.6×10^{-3} mol dm^{-3}. The temperature range is 293–313 K.

Tacke and Vorlop [21] determined the kinetics of nitrate hydrogenation over the Pd/Cu bimetallic catalyst containing 5 wt % of Pd and 1.25 wt % of Cu. The measurements were performed in a slurry reactor at 293 K. They found the reaction rate to be of 0.7 order with respect to nitrate and independent of the hydrogen partial pressure provided that this pressure is higher than about 1 bar.

Warna et al. [11] performed measurements in a metallic monolith reactor. They suggested that, in the process of catalytic nitrate reduction, the key intermediate on a noble metal might be NO. According to that mechanism, a kinetic model that accounts for a stepwise transformation of the parent ion via different intermediates to nitrogen and ammonia was derived.

Ilinitch et al. [12] claimed that NO is the key intermediate in hydrogenation of NO_3^- and NO_2^- in the conversion of NH_{ads} species on the surface.

Pintar et al. [10] presented kinetic data on the reduction of NO_3^- and NO_2^- over $Pd–Cu/Al_2O_3$ catalysts. The kinetic data were interpreted with rate equations based on the Langmuir–Hinshelwood mechanism. The reduction of nitrate occurs by heterolytic electron transfer between adsorbed reactant species on different types of active sites.

However, in these papers no information is given about the activation energy. With the aim of gaining a deeper understanding of the mechanism of nitrate

Rate constants of nitrate hydrogenation for different temperatures and values of activation energy

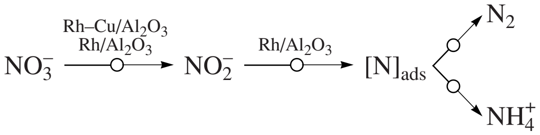
Catalyst	$k \times 10^4$, dm^3/(mol s)					E_a, kJ/mol
	293 K	298 K	303 K	308 K	313 K	
5% Rh/Al_2O_3	5	8	13	14	17	44
5% Rh/Al_2O_3 + 1.5% Cu/Al_2O_3	6	9	14	16	17	42
5% Rh–1.5% Cu/Al_2O_3	21	27	40	44	46	31

reduction on bimetallic rhodium based catalysts, we studied the kinetics of nitrate hydrogenation over 5% Rh/Al_2O_3, the physical mixture of 5% Rh/Al_2O_3 and 1.5% Cu/Al_2O_3, and the bimetallic catalyst containing also 5 wt % of rhodium and 1.5 wt % of copper. Kinetic measurements were performed in a slurry reactor at atmospheric pressure and at a different reaction temperatures (293, 298, 303, 308, and 313 K).

On the basis of the experimental data, we found that the reaction order with respect to NO_3^- was about one for all studied catalysts. Kinetic studies carried out at three different temperatures allowed calculating the activation energy for each system (table). E_a values presented in the table show small differences of this parameter determined for monometallic 5% Rh/Al_2O_3 and bimetallic 5% Rh – 1.5% Cu/Al_2O_3 systems.

It is generally accepted that the hydrogenation of NO_3^- is a consecutive reaction with NO_2^- as an intermediate product, and the hydrogenation of NO_2^- is a key step in determining selectivity for N_2 and NH_4^+ [3, 9, 14]. In the case of Pd–Cu/Al_2O_3 [10] and Pt–Cu/Al_2O_3 [25] catalysts, it was shown that the first step in the nitrate reduction is probably a redox reaction between Cu^0 and NO_3^-, leading to nitrite intermediates and to an oxidized form of copper. The role of noble metal is the reduction of nitrite to N_2 or NH_4^+ by catalytic reduction and the activation of hydrogen, allowing the reduction of Cu^{2+} to Cu^0. However, monometallic palladium and platinum catalysts are inactive for nitrate reduction [10, 25].

In the present study, it was shown that the monometallic rhodium catalyst is active in the reduction of NO_3^-, but its activity is smaller than bimetallic Rh–Cu/Al_2O_3 catalysts (Fig. 1). In the case of the Rh–Cu bimetallic system, the reduction of NO_3^- can take place on a mixed site, where both components of the Rh–Cu/Al_2O_3 catalyst participate in the catalytic transformation. The promoting effect of copper can be related to its ability to reduce nitrate according to the redox reaction. The intermediate products formed during the process undergo further reduction on rhodium according to a classic catalytic reaction. On the other hand, we found that the activity of the monometallic rhodium catalyst is also high and the studied reaction proceeds as a classic catalytic reaction. Because of the small differences of apparent activation energy obtained for monometallic and bimetallic systems, it is difficult to choose the appropriate mechanism of NO_3^- reduction in the presence of the 5% Rh–1.5% Cu/Al_2O_3 catalyst. It seems that the reduction of NO_3^- over bimetallic catalysts can take place according to the following scheme:



In the case of using a physical mixture of the 5% Rh/Al_2O_3 and 1.5% Cu/Al_2O_3 catalysts in catalytic measurements, the activation energy shows a value between the ones calculated for the mono- and bimetallic systems, which is 42 kJ/mol. Carrying out a catalytic process of NO_3^- hydrogenation in a slurry reactor in the presence of a physical mixture of monometallic catalysts, one can expect the separation of its components; however, we cannot eliminate the presence of a certain amount of catalyst where both metallic components are in close contact. In such a situation, the reaction will run in parallel according to two different mechanisms. The E_a value, however, is closer to the one obtained for the 5% Rh/Al_2O_3 system. Therefore, it can be assumed that the classic catalytic mechanism is the dominant process in this case.

CONCLUSIONS

The monometallic rhodium catalyst (5% Rh/Al_2O_3) is characterized by high activity and high selectivity toward N_2 in the reduction of nitrates. The addition of copper insensibly increases activity but does not improve the selectivity toward nitrogen.

The apparent activation energies calculated for the mono- and bimetallic systems and also for a physical mixture do not differ markedly.

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