

CHEMICAL KINETICS
AND CATALYSIS

Kinetics of the Reduction of *p*-Nitrobenzoic Acid Esters in Nanoreactors on the Basis of Sulfonated Polymers

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Abstract—The kinetics of the reduction of *p*-nitrobenzoic acid esters in nanoreactors based on sulfonated network polymers containing nanodispersed palladium was studied. The kinetic characteristics of the hydrogenation of aromatic nitro compounds were calculated.

Keywords: nanoreactor, network polymers, *p*-nitrobenzoic acid esters, hydrogenation.

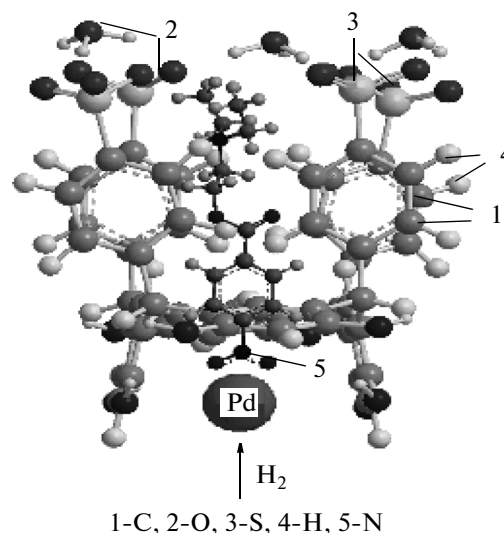
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INTRODUCTION

Liquid-phase hydrogenation of aromatic nitro compounds on heterogeneous catalysts was considered in many papers [1, 2], but studies on optimization of the process are still under way. The results of fundamental research at the international level showed [3] that the heat transfer and the mutual transport of reactant molecules are multiply accelerated in small reactors (nanoreactors). This leads to a drastic increase in the rate and selectivity of chemical transformations, making it possible to create high-performance and waste-free technologies. We showed that a solid-phase nanoreactor can be created on the basis of sulfonated polycalixresorcinarene [4, 5]. The use of sulfonated polycalixresorcinarene as a nanoreactor for the synthesis of biologically active compounds is of interest.

The derivatives of *p*-aminobenzoic acid from the group of benzocaine–novocaine–dicaine play an important role among synthetic anesthetics [6]. The key stage of their synthesis is the reduction of the nitro group to the amino group. In chemical pharmaceutical industry, the drugs of the benzocaine–novocaine series and their precursors are still prepared by the reduction of *p*-nitrobenzoic ethers with iron. This leads to multistage purification of the intermediates and final products and decreases the yield of the products that satisfy the pharmacopoeial requirements. Therefore, studies of the hydrogenation of *p*-nitrobenzoic acid derivatives are important. The reduction of *p*-nitrobenzoic acid esters in a nano-

reactor based on sulfonated polycalixresorcinarene is shown in the scheme below:



In this study, we investigated the hydrogenation of nitrobenzene; *p*-nitrobenzoic acid; and methyl, ethyl, and propyl *p*-nitrobenzoic acid esters in nanoreactors based on network sulfonated polymers (sulfocationite KU-23 30/100, sulfonated polycalixresorcinarene) containing palladium nanoparticles:



where R = H, COOH, COOCH₃, COOC₂H₅, COOC₃H₇.

EXPERIMENTAL

Sulfonated polycalixresorcinarene was prepared as spherical granules with a diameter of 0.01–0.05 cm by

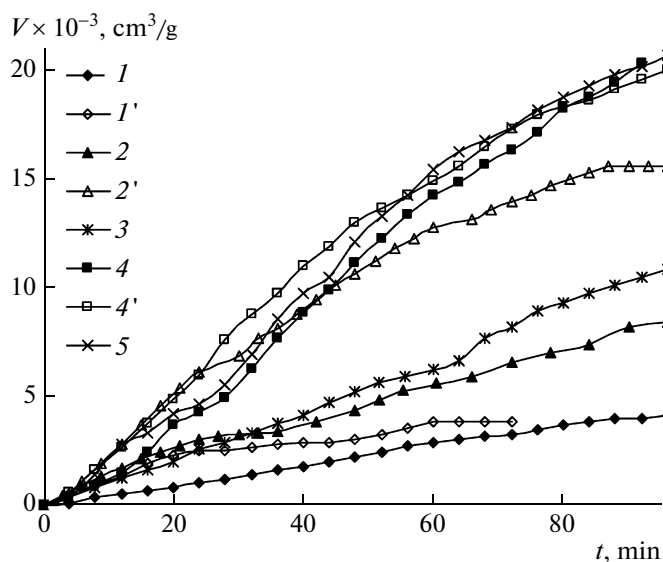


Fig. 1. Time dependences of hydrogen absorption during the reduction of nitro compounds in the presence of palladium-containing (*I*–*5*) sulfonated polycalixresorcinarene and (*I'*, *2'*, *4'*) KU-23: (*I*, *I'*) *p*-nitrobenzoic acid; (*2*, *2'*) nitrobenzene; (*3*) methyl, (*4*, *4'*) ethyl, and (*5*) propyl *p*-nitrobenzoic acid esters.

the procedure [4]. Sulfonated polycalixresorcinarene has a gel structure containing two kinds of ionogenic groups—phenolic OH and SO₃H groups. The total dynamic ion-exchange capacity is 5.65 mg-equiv/g of the polymer H form; the sulfo group capacity is 2.45 mg-equiv/g [7]. The macroporous sulfocationite KU-23 30/100 contains SO₃H groups; its total ion-exchange capacity is 3.8 mg-equiv/g of the polymer H form [8].

Kinetic characteristics of the hydrogenation of nitro compounds in the presence of sulfonated polycalixresorcinarene and sulfocationite KU-23 30/100 at 308 K

Compound	q_{O8}	q_{O14}	$a \times 10^3$	E
Sulfocationite KU-23 30/100				
ArNO ₂	−0.445	−0.445	10.7 ± 0.6	—
C ₂ H ₅ OOCArNO ₂	−0.436	−0.432	11.2 ± 1.5	24.4
HOOCArNO ₂	−0.430	−0.431	2.7 ± 1.0	32.8
Sulfonated polycalixresorcinarene				
ArNO ₂	−0.445	−0.445	4.9 ± 0.8	22.5
CH ₃ OOCArNO ₂	−0.430	−0.435	3.7 ± 0.5	45.0
C ₂ H ₅ OOCArNO ₂	−0.436	−0.432	7.0 ± 1.0	38.3
C ₃ H ₇ OOCArNO ₂	−0.433	−0.436	8.1 ± 1.8	29.7
HOOCArNO ₂	−0.430	−0.431	1.2 ± 0.2	25.7

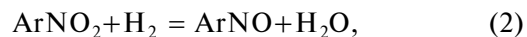
q_i is the charge on the *i*th atom; a is the catalytic activity, mol of H₂/(min g of Pd); and E is the activation energy, kJ/mol.

The polymers containing nanodisperse palladium were prepared by the procedure [9]. The palladium content in the polymers was 0.02 g per 1 g of dry polymer; the dispersity of metallic palladium was 25 ± 5 nm according to XRD data [9].

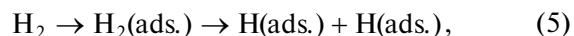
Reaction (1) was studied at a gas pressure of 1.013×10^{-5} Pa at temperatures of 303–328 K. Hydrogenation was performed by the procedure [10]. To prevent the side process of re-esterification, methyl, ethyl, and propyl esters were hydrogenated in methanol, ethanol, and propanol, respectively. Nitrobenzene was hydrogenated in ethanol; *p*-nitrobenzoic acid was hydrogenated in water at 338 K. The activation energy was calculated by the Van't Hoff equation. The atomic charges were calculated using the MOPAC-2009, Chem3DUltra program and the Wang–Ford procedure.

RESULTS AND DISCUSSION

As is known, reduction (1) of aromatic nitro compounds occurs in three stages [11]:



Reaction (2) was assumed to be the limiting stage of process (1). Then the transformation rate is probably determined either by the slow recombination of the adsorbed hydrogen molecule



or by the diffusion of the reactant components for collision with the catalyst in the polymer phase.

Let us consider both mechanisms of (1). The diffusion and process (5) are characterized by different activation energies. For (5), the activation energy is expected to be comparable to the H–H bond cleavage (432 kJ/mol [12]). Figure 1 shows the kinetic curves of the reduction of nitrobenzene, *p*-nitrobenzoic acid, and methyl, ethyl, and propyl *p*-nitrobenzoic acid esters in the presence of palladium-containing network polymers (sulfocationite KU-23 30/100 and sulfonated polycalixresorcinarene) at 308 K. The characteristics of the hydrogenation of the nitro compounds on palladium-containing polymers at 308 K are presented in the table. The kinetic characteristics (Fig. 1 and table) of (1) show that the hydrogenation of the nitro group in *p*-nitrobenzoic acid esters occurs at high rates under mild conditions. At a gas pressure of 1.013×10^{-5} Pa and a temperature of 308 K, the catalytic activity of palladium-containing network polymers is 1.2×10^{-3} to 11×10^{-3} mol of H₂/(min g of Pd). The activation energy is 35 ± 10 kJ/mol (table).

According to our experimental data, the reduction of nitro compounds in the presence of polymer nanocomposites containing nanodisperse palladium is a first order process with respect to hydrogen. Palladium remains at the zero oxidation level during hydrogenation.

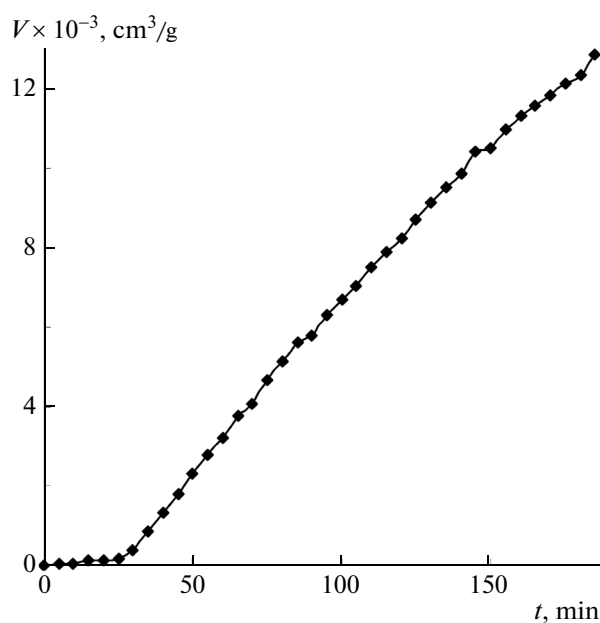


Fig. 2. Time dependence of hydrogen absorption during the reduction of nitrobenzene in the presence of palladium-containing sulfonated polycalixresorcinarene at 313 K.

tion. The catalytic activity of the nanocomposites under study is comparable to that of crystalline palladium particles fixed on the carbon surface in the reduction of trifluoromethylnitrobenzene [1] conducted under similar conditions. The catalytic activity of the nanocomposites did not decrease and the Pd-containing polymers had no signs of mechanical destruction after 5000 hydrogenation cycles. According to Fig. 1 and the table, the catalytic activity was higher on KU-23. The macroporous structure of KU-23 leads to the higher rate of the delivery of the reagents (nitroaromatic compounds and hydrogen) to the catalyst than on sulfonated polycalixresorcinarene.

The formal kinetics does not allow us to distinguish the first order chemical reaction from diffusion [13]. The diffusion mechanism follows from the low activation energy and the relatively high catalytic activity on KU-23. The kinetic curve (Fig. 2) shows an induction period during the reduction of nitrobenzene in the presence of sulfonated polycalixresorcinarene, which is probably necessary for the diffusion delivery of the object of hydrogenation to the catalyst.

To determine the mechanism of hydrogenation, we considered hydrogen absorption to high degrees of conversion. Figure 3 shows the kinetic curves of prolonged hydrogenation of ethyl *p*-nitrobenzoic acid ester in ethanol at 313 K on palladium-containing network polymers. When the process was interrupted, hydrogen delivery to the reaction medium stopped and the chemical reaction was discontinued. However, the diffusion of reagents in the polymer phase continued. According to Fig. 3, the initial rate of hydrogenation

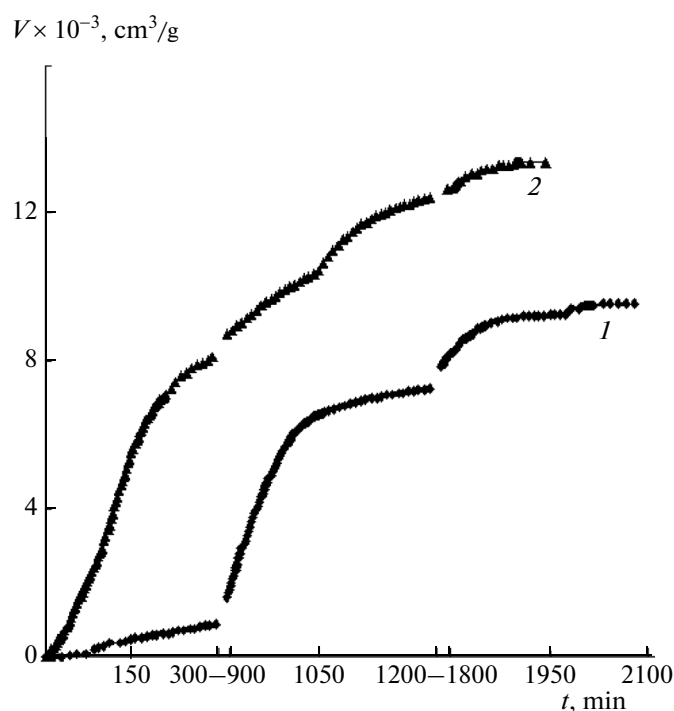
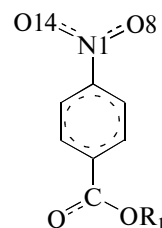


Fig. 3. Time dependences of hydrogen absorption during the reduction of ethyl *p*-nitrobenzoic acid ester in ethanol in the presence of palladium-containing sulfonated network polymers on (1) sulfonated polycalixresorcinarene and (2) KU-23.

was higher after each interruption than before it. The reaction rate is evidently limited by diffusion.

Let us consider the kinetics of the process from the viewpoint of the chemical reaction rate. The hydrogenation of the nitro group attached to the aromatic ring is a nucleophilic substitution reaction. The nitro group, which is one of the strongest electron-accepting groups, is the object of the nucleophilic attack and can effectively delocalize the negative charge that lies mainly in the *ortho*- and *para*-positions of the benzene ring. The nucleophilic reagent in our case is the hydrogen atom adsorbed by the catalyst surface (Eq. (5)) and carrying excess electron density. In aromatic compounds, the nitro group affects the electron density distribution due to the induction and especially mesomeric effects, changing the electron-acceptor ability of the nitro compounds. An increase in the effective negative charge on the oxygen atoms of the nitro group should cause an increase in the hydrogenation rate. The table shows the substituent effects on the electron density distribution in *p*-nitrobenzoic acid esters



where R_1 is H, CH_3 , C_2H_5 , or C_3H_7 . According to the table, the decrease in the electron density on the oxygen atom of the nitro group on passing from nitrobenzene to *p*-nitrobenzoic acid is related to the lowest catalytic activity during the reduction of *p*-nitrobenzoic acid. The catalytic activity of palladium-containing sulfonated polycalixresorcinarene increases as the mass of the substituent increases in the series CH_3 , C_2H_5 , C_3H_7 . The rate of hydrogenation of *p*-nitrobenzoic acid esters by reaction (1) is probably limited by both the diffusion and the chemical reaction. The reaction kinetics may be mixed.

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