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Characteristic Features of the Selective Action of Platinum-Doped Glass Fiber Woven Catalysts in the Liquid-Phase Reduction of Polyfunctional Aromatic Nitro Compounds

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The kinetics of liquid-phase hydrogenation of trinitrotoluene and trinitrobenzene on platinum-doped (up to 0.2 wt %) glass fiber woven catalysts (SiO₂ content of up to 98 wt %, specific surface area of 1–15 m²/g) was studied for the first time. Powdered carbon-supported palladium (palladium content of 5 wt %, specific surface area of up to 500 m²/g), which is a traditional catalyst for these processes, was used as the reference material.

The glass fiber catalysts were found to exhibit a much higher activity than the traditional powder systems. Unexpectedly, these catalysts were found to be exceptionally selective toward successive hydrogenation of nitro groups; in particular, the first nitro group is reduced at a rate an order of magnitude higher than the second nitro group and, in turn, the third nitro group is reduced more slowly than the second one by about an order of magnitude. The hydrogenation on the traditional Pd/C powder system involves synchronously all the nitro groups, i.e., proceeds almost nonselectively.

This result opens up a new way for industrial production of complex aromatic nitroamines in a one-step process. This process can be used as an industrial base for utilization of nitroaromatic explosives eliminated from normal use to obtain useful products.

The first studies of the mechanism and kinetics of liquid-phase hydrogenation of nitroaromatic compounds on new-generation catalytic systems, namely, glass fiber woven catalysts (GWCs) doped by platinum group metals, were carried out only several years ago [1-3]. The simplest monofunctional nitroaromatic compound, nitrobenzene, which is catalytically reduced by hydrogen to aniline, was chosen as the basic

investigation object. The studies cited demonstrated that the GWC systems possess a much higher specific catalytic activity than the traditional powder Pd/C catalysts. Physicochemical studies of the glass fiber silicate supports of the active phase led researchers [4–6] to the conclusion that the abnormally high activity of a GWC system is related to the amorphous coordinatively defective state of the glass template, the specific structure of the silanol groups formed in it, and the specific mechanism of attachment of atomic clusters of catalytically active metals to the metastable glass fiber support. The technological advantages of GWCs when used in the catalytic hydrogenation of aromatic nitro compounds were patented [7].

This paper is a next step in the study of the characteristic features of reduction of nitroaromatic compounds on GWC systems. Hydrogenation of polyfunctional aromatic compounds, in particular, the reduction of trinitrotoluene and trinitrobenzene to amines on platinum-activated glass fiber woven catalysts, was chosen for the investigation.

The GWC samples were prepared using glass fiber woven materials fabricated as a sparse mesh or a linenwoven cloth as supports. The elementary fiber diameter was 7–9 μ m. These articles were manufactured from traditional silicate glasses in which the content of silicon dioxide varied from 55 to 98 wt %, while the remaining components were usual for glass silicate compositions of the alumina, magnesia, calcium oxide, and boron oxide series (glass fiber fabrics manufactured at the Polotsk Steklovolokno Production Association were used as the starting materials to prepare the catalysts).

The catalytically active component (in this study, platinum) was introduced into the glass fiber template via ion exchange processes during impregnation of the support in aqueous solutions of platinum-containing salts followed by drying and heat treatment of the samples. The platinum content in the samples ready for experiments varied from 0.1 to 0.2 wt %. The catalyst porosity (the degree of development of the internal sur-

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Fig. 1. Degree of hydrogen conversion vs. transformation time during the TNT hydrogenation.

face) ranged from 1 m²/g (for samples manufactured from silica fabrics) to 15 m²/g (for samples manufactured from alumina–borosilicate glass fiber fabrics). The specified value of this parameter was ensured by preliminary dosed leaching of the starting glass fiber materials in acid media.

The experiments were carried out in static (nonflow) setups in 50- to 200-mL laboratory glass reactors. The reaction medium was formed as a 1-3% solution of trinitrotoluene (trinitrobenzene) in isopropanol. A reactor with a shaking device that ensured stirring of the reaction mixture through the to-and-fro motion of the whole reaction vessel was used. The rocking amplitude was 8-10 cm and the frequency was 500 swings per minute. Hydrogen was supplied through a nonflow circuit from a calibrated receiver with a water seal. This allowed us to record the kinetics of transformation of the nitroaromatic compound by measuring the rate of hydrogen absorption with time. A piece of the woven glass fiber catalyst was situated in the reactor in the free (nonfastened) state and was in active contact with the liquid due to the turbulent conditions created in the reactor by the shaker. The weight of the catalyst loaded into the reactor was about 0.08–0.1 g per milliliter of the working solution.

In addition to the recording of the dynamics of hydrogen absorption, the kinetics of hydrogenation was measured by taking samples of the working fluid from the reactor. The samples were analyzed for reactants and products (nitroamines and amines). The intermediate compounds and the reaction products, as well as their elemental composition, were identified by ¹H NMR using a Bruker AC-200P spectrometer (¹H, 200 MHz). The analytical procedure used in the work allowed us to detect the following transformation products: 4-hydroxylamino-2,6-dinitrotoluene (2ADNT), 4-amino-2,6-dinitrotoluene (2A4HANT), 2-hydroxylamino-4-amino-6-



Fig. 2. Rate of hydrogen absorption vs. degree of hydrogen conversion during the TNT hydrogenation.

nitrotoluene (2HA4ANT), 2,4-diamino-6-nitrotoluene (2,4DANT), 2,4-diamino-6-nitrosotoluene (2,4DANST), 2,4-diamino-6-hydroxylaminotoluene (2,4DAHAT), and 2,4,6-triaminotoluene (TAT).

To compare the key parameters of trinitrotoluene (trinitrobenzene) hydrogenation on GWC systems with the process parameters of hydrogenation on a dispersed Pd/C catalyst under standard conditions, control experiments were carried out. Catalyst samples resembling industrial catalysts in their characteristics were prepared: a carbon powder with a particle size of 100–200 μ m, an internal surface area of 500 m²/g, and a Pd content of 5 wt %.

Figure 1 presents experimental data characterizing the hydrogen absorption dynamics during hydrogenation of trinitrotoluene (TNT) over various catalysts (the dynamic course of trinitrobenzene reduction is qualitatively similar).

Curve 1 describes the absorption of hydrogen in TNT hydrogenation on a GWC sample with a specific surface area of $1 \text{ m}^2/\text{g}$. The dashed line designates the integral amount of absorbed hydrogen, which corresponds to the complete stoichiometric reduction of the three nitro groups to amino groups. The data presented in Figure 1 demonstrate that the kinetic curve is stepwise: after absorption of one-third of the hydrogen (complete reduction of the first nitro group, with a characteristic time of 30 min), hydrogenation is sharply retarded; then the second nitro group starts to be hydrogenated, and this process lasts for 3 h. This is followed by hydrogenation of the third nitro group, which develops much more slowly than the second step.

These macrokinetic regularities identified using the integral volumetric recording of the reaction dynamics were confirmed by NMR monitoring of the composition of the reaction medium. The interpretation of the NMR spectra showed that, after the first step of hydrogen absorption (~2.3 mol, which makes up one-third of the whole amount of hydrogen needed for complete reduction of the three nitro groups), the reaction mixture contains only 4HADNT, 2ADNT, and 4ADNT. The compounds identified after the second hydrogenation step (~6.11 mol of hydrogen) were 2,4DANT, 2A4HANT, 2HA4ANT, 2,4DANST, and 2,4DAHAT. The third step (~8.4 mol of hydrogen absorbed) yields TAT and 2,4DANT. These results indicate that the reduction of trinitrotoluene on platinum-activated GWCs proceeds by a complex stepwise mechanism involving successive hydrogenation of the nitro groups.

This conclusion becomes more evident when the results are presented in the coordinates current transformation rate-specific fraction of hydrogen absorbed (Fig. 2). It can be seen that the GWC sample with a specific surface area of $1 \text{ m}^2/\text{g}$ (curve 1) reduces the first nitro group at a rate 6-7 times higher than it reduces the second nitro group and 60-70 times higher than the third nitro group is reduced to an amino group. These data indicate unambiguously that the selectivity of TNT hydrogenation on GWC systems is extremely high and allows one-step preparation of any combination of amines and nitroamines according to a specified task. For comparison, Figs. 1 and 2 (curves 4) show the kinetics of reduction of TNT nitro groups on traditional 5% Pd/C powder catalysts (the experimental conditions and the specific amount of the catalytic metal in the experiments shown by curves 1 and 4 are identical). The pattern of TNT transformation on 5% Pd/C and the data of NMR analysis of the reduction products on this catalytic system demonstrate substantial differences: the powder catalyst accomplishes an almost nonselective reduction of TNT, the three nitro groups being hydrogenated almost synchronously up to complete transformation into amino groups.

When analyzing the possible mechanism of the hyperselectivity discovered for the GWC system in TNT hydrogenation, we put forward a hypothesis relating this effect to the presence of two different valence states of platinum, Pt⁰ and Pt²⁺, in the GWC. There are grounds for assuming that this composition of active sites can ensure selective coordination of trinitrotoluene adsorbed on the GWC surface. In the case of traditional powder catalysts, only Pt⁰ participates in the process. This results in planar TNT adsorption, which ensures equal accessibility of all three nitro groups for the reaction with hydrogen. A role of the substantial difference between the specific surface areas of the new and the traditional catalytic systems $(1 \text{ m}^2/\text{g for the})$ GWC and 500 m²/g for the powder catalyst) in the high selectivity of TNT hydrogenation also cannot be ruled out. This version implies that the steric factor is more pronounced on the catalyst with the small surface area, and, hence, the coordination of the TNT nitro groups in the adsorbed state is highly differentiated. In the catalyst sample with the developed surface, the TNT molecule penetrates into the near-surface layer and is localized inside a pore, resulting in equalization of the coordination factor for all nitro groups.

For experimental verification of this hypothesis, we prepared GWC samples with developed surfaces, 5 and 15 m²/g. The kinetics of TNT hydrogenation on these catalyst samples is shown by curves 2 and 3 (Figs. 1, 2). The experiment confirmed qualitatively the assumption; i.e., the selectivity coefficients decrease with an increase in the specific surface area. On passing from the 1 m²/g GWC sample to the 15 m²/g GWC, the selectivity coefficients for the second nitro group decrease from 6–7 to 2–3, while those for the third nitro group decrease from 60–70 to 25–35. However, the porous GWC still remains highly selective compared to the traditional powder catalysts, which have much more developed surfaces (500 m²/g).

This study represents the first stage in investigating the mechanism of hyperselectivity discovered in hydrogenation of polyfunctional nitroaromatic compounds on glass fiber woven catalysts doped with platinum group metals. It is necessary to study the specific features of action of GWCs activated by various metals and metal compositions for different contents of these metals in the glass template (Pt, Pd, Rh, Ru). It is important to study in more detail the role of the specific surface area of the GWC in the hydrogenation of nitroaromatic compounds. Nevertheless, the practical value of this study, which opens the way for one-step synthesis of complex nitroamines, is already obvious. Moreover, this process should be regarded as the foundation for the development of industrial processes for utilization of nitroaromatic explosives to give useful products for civilian purposes.

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