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The effect of preparation conditions of Pd/C catalyst on its activity and selectivity in the aqueous-phase hydrogenation of 2,4,6-trinitrobenzoic acid

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ABSTRACT

The effect of the nature of alkaline agent and pH value of hydrolysis of Pd(II) chloride complex into palladium polynuclear hydroxo complexes, as precursor of active component in Pd/C catalyst, on the dispersion of palladium particles supported on carbon material Sibunit was revealed. It was shown that an increase in the particle size of supported palladium enhances the specific catalytic activity in hydrogenation of 2,4,6-trinitrobenzoic acid and changes the direction of the transformation (increases the fraction of non-aromatic intermediate, cyclohexane-1,3,5-trione trioxime, in the products). The results obtained are essential for optimizing the particle size of supported palladium in selective hydrogenation of polyfunctional organic compounds.

1. Introduction

Catalytic hydrogenation of aromatic trinitro compounds is of practical importance for utilization of explosives and synthesis of various useful chemical products [1–3]. The application of this method for safe deactivation of 2,4,6-trinitrotoluene (TNT), which is among the most widespread explosives, has significant environmental advantages over its utilization by blasting, combustion, biological degradation or chemical reduction. Difficulties with the catalytic process, which are caused by a strong adsorption of aromatic trinitro compounds and their conversion products on the surface of metal catalysts as well as by a high exothermic effect of the reduction to triamine, initiate studies on optimization of the reaction conditions and synthesis of advanced catalytic systems that are highly selective in the reduction of the substrate to triamine.

Catalytic hydrogenation of aromatic trinitro compounds is commonly performed in an organic solvent medium (dioxane, ethyl acetate, low-molecular alcohols) at elevated hydrogen pressure and constant removal of heat released in the reaction. The reaction is catalyzed by Raney Ni [2–9], PtO_2 [10–13] as well as Ni, Pd, Pt, Ru, Rh and polymetallic compositions deposited on activated carbon, SiO_2, Al_2O_3 or other supports [12,14–19]. It was found that the direction of reductive transformations is determined by hydrogenation conditions and by the catalyst composition and structure. However, the attempts to reveal the relations between reaction rate, composition of hydrogenation products, particle size of supported metal and its electronic state are quite scarce [16–19].

Among aromatic trinitro compounds, the most available and promising for further processing is the 2,4,6-trinitrobenzoic acid (TNBA) produced by TNT oxidation. The reduction of TNBA yields such valuable chemical products as 1,3,5-triaminobenzene (TAB) and 1,3,5-trihydroxybenzene (phloroglucinol) [20–26]. The main technological advantage of TNBA is the good water solubility of

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its alkali metal salt [22], which makes it possible to run the reaction in such non-toxic and inexpensive solvent. Publications on the reduction of TNBA are focused mostly on a search for optimal conditions of selective TAB formation, whereas information on the effect of aqueous-phase hydrogenation conditions and catalyst composition on the rate and direction of TNBA transformations is absent. In our earlier works [27–29], the reaction conditions were optimized, and compounds produced by the multistep aqueous-phase hydrogenation of TNBA on Pd/C catalyst were identified by NMR.

The present work aims to reveal the effect of the synthesis conditions of Pd/C catalyst on the nanoparticles (NPs) size of supported palladium and its properties in hydrogenation of TNBA. A mesoporous material Sibunit [30–33] was chosen as the carbon support. The absence of micropores and the developed mesopore space make the entire surface of the support accessible to anchoring of palladium and adsorption of large organic molecules, while a relative chemical inertness prevents undesirable side reactions. High mechanical strength of this carbon material is also essential under vigorous stirring. During the catalyst synthesis, in order to regulate the size of supported palladium NPs and their localization, we used the hydrolytic precipitation of palladium polynuclear hydroxo complexes (PHC) with variation of the nature of alkaline agent and pH value of hydrolysis.

In the present work, the reaction products were identified based on the NMR spectroscopy data. The efficacy of application of the NMR technique in analyzing the products of hydrogenation of aromatic trinitro compounds was reported earlier [19,25,27–29]. The choice of this method is explained mainly by its high informativity and non-destructive nature. Moreover, other analytical techniques are characterized by either low efficiency or application irrelevance. For instance, gas chromatography-mass spectrometry or high-performance liquid chromatography should be considered unsuitable for this analytical task because of low stability of the compounds under investigation as well as the absence of reference compounds and published mass spectra for the majority of these compounds.

2. Experimental

2.1. Catalysts preparation and characterization

5% Pd/C catalysts were synthesized by hydrolytic precipitation of palladium PHC on the surface of carbon material Sibunit (prepared according to [31] at the Department of Experimental Technologies, Institute of Hydrocarbons Processing SB RAS, S_{BET} 422 $m^2 g^{-1}$). The grain size of the carbon support was 50–140 μm. An initial aqueous solution of $H_2[PdCl_4]$ was prepared by dissolution of $PdCl_2$ in concentrated hydrochloric acid (the Pd to HCl molar ratio of 1:2) and dilution with water to a desired concentration of Pd. In the synthesis, an alkaline precipitant was added dropwise to the $H_2[PdCl_4]$ aqueous solution until a specified pH value was attained. The pH value was controlled on a SevenMulti (Mettler Toledo) instrument using a combined electrode. The resulting deep brown solution of PHC was mixed with an aqueous suspension of Sibunit. This was accompanied by a complete adsorption of the complexes with discoloration of the solution. PHC were synthesized upon variation of the pH of precipitation (from 4 to 5 units) and the composition of precipitant (KOH, K_2CO_3, $KHCO_3$, NaOH, Na_2CO_3, $NaHCO_3$, LiOH, Li_2CO_3). A further liquid-phase reduction of palladium on the surface of support was performed with sodium formate in an alkaline medium [34]. After the reduction of palladium, the obtained samples were washed with water to pH 7, filtered and stored moist (the moisture content of ca. 50%). Before further experiments, no any pretreatment of the obtained catalyst was performed.

Metal content of Pd/C catalysts was measured by atomic absorption spectrometry (AAS) on a AA-6300 (Shimadzu) instrument with combustion of the samples in a muffle furnace at a temperature of 823 K and dissolution of the residues.

Palladium dispersion was determined by CO pulse chemisorption at room temperature on an AutoChem II 2920 (Micromeritics) analyzer equipped with a thermal conductivity detector (TCD). Pretreatment of the catalysts before measurements included exposure in a 10 vol.% H_2 – Ar medium under temperature-programmed reduction (TPR) to 393 K with subsequent cooling in flowing argon. The TPR pretreatment allowed recording the hydrogen adsorption-desorption profiles. The values of metal dispersion were calculated from the stoichiometry CO/Pd = 1 [35].

The palladium dispersion *D* was recalculated to the volume-area mean diameter of NPs assuming spherical shape as described in [36,37]:

$$\langle d \rangle_{vs,CO} = \frac{6 \upsilon_M}{a_M D} \tag{1}$$

where υ_M is the volume occupied by an atom in bulk metal (0.0147 nm^3 for Pd), and a_M is the area occupied by a surface atom (0.0793 nm^2 for Pd).

Transmission electron microscopy (TEM) images were recorded on a JEM-2100 (JEOL) electron microscope with a lattice resolution 0.14 nm and accelerating voltage 200 kV. Samples were prepared as ethanol suspensions and deposited on the perforated carbon-coated copper grids, which were then introduced into the electron microscope chamber. TEM images were analyzed using DigitalMicrograph (Gatan) software.

The volume-area mean diameter of NPs was determined by measuring the size of more than 350 NPs for each sample and calculating by the equation [36,37]:

$$\langle d \rangle_{vs} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{2}$$

where n_i is the number of NPs counted in the intervals of mean diameter d_i.

2.2. Hydrogenation of TNBA

TNBA (98% purity) was synthesized by the oxidation of TNT as reported in [38]. The sodium salt of TNBA was obtained by the addition of sodium bicarbonate (0.59 g) to the aqueous suspension of TNBA (2.00 g) until its complete dissolution and a cessation of CO_2 release [22]. The catalytic hydrogenation of the obtained salt (100 mL of 2% aqueous solution) was performed at a temperature of 323 K and pressure of 0.5 MPa in the presence of 100 mg (dry) catalyst (the loading was about 400 g of TNBA per 1 g of Pd). The reaction was conducted in a 180 mL steel autoclave equipped with a valve for hydrogen input and an external thermostatted jacket. The reaction mixture was stirred by a magnetic stirrer at 1400 rpm to prevent external diffusion limitations. The progress of the reaction was monitored by measuring the volume of consumed hydrogen with a mass flow meter. After completion of the reaction (cessation of hydrogen consumption) and cooling, the sampling was carried out with a syringe.

The catalytic activity was expressed as the turnover frequency (TOF) calculated by the equation

$$\mathrm{TOF} = \frac{r(H_2)}{m C_s} \tag{3}$$

where $r(H_2)$ is the reaction rate measured 5 min after its onset, i.e. on the linear region of the hydrogen consumption curve (mol H_2

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