



International Conference on Oil and Gas Engineering, OGE-2016

## A study of Pd/C catalysts in the liquid-phase hydrogenation of 1,3,5-Trinitrobenzene and 2,4,6-Trinitrobenzoic acid. Selection of hydrogenation conditions for selective production of 1,3,5-Triaminobenzene

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### Abstract

The liquid-phase hydrogenation of aromatic trinitro compounds was studied at atmospheric and elevated pressure and a temperature of 50–70 °C. It was shown that at atmospheric pressure, irrespective of the solvent type (water or acetic anhydride), a complete reduction of the nitro groups of 2,4,6-trinitrobenzoic acid to amino groups does not occur; the intermediate products of hydrogenation and the products of secondary transformations are present in the solution. An increase in pressure to 5 bars ensures a complete hydrogenation of 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene with the formation of 1,3,5-triaminobenzene.

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Peer-review under responsibility of the Omsk State Technical University

**Keywords:** catalytic hydrogenation; 1,3,5-Trinitrobenzene; 2,4,6-Trinitrobenzoic acid; 1,3,5-Triaminobenzene; Pd/C

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## 1. Introduction

Catalytic hydrogenation of aromatic trinitro compounds is of interest for the development of theoretical bases of the liquid-phase hydrogenation of organic compounds and has practical value in utilization of explosives. Safe deactivation of one of the most widespread explosives, 2,4,6-trinitrotoluene (TNT), by this method has significant advantages over its utilization by blasting, burning or chemical reduction in terms of detrimental environmental outcome. So, the topical lines of investigation include optimization of the catalytic process conditions and development of more efficient catalysts. The reduction of all nitro groups can produce 2,4,6-triaminotoluene, which is an essential component for the synthesis of a wide range of civil products [1].

A scheme of TNT hydrogenation is a complex chain of consecutive and parallel reactions [2–4], which can hardly be described due to difficult identification of intermediate compounds. Along with TNT, among the most available and promising trinitro compounds are 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrobenzoic acid (TNBA) [5–9]. TNB is a product of decarboxylation of TNBA, while TNBA can be obtained by oxidation of TNT. The direct use of TNBA as the substrate for aqueous-phase hydrogenation is limited by low solubility in water. However, as a component of a salt with alkaline metals this compound has a good solubility in water [7]. The performance of hydrogenation in aqueous solutions ensures environmental benefit for the synthesis of aromatic amines from TNBA. Information about the effect produced by conditions of the aqueous-phase hydrogenation on the process rate and depth is virtually absent in the literature.

The work was aimed at selecting such conditions (pressure, temperature and solvent) of the hydrogenation that would provide an exhaustive reduction of all nitro groups of TNB and TNBA with the use of the 6 % Pd/C catalyst.

## 2. Experimental

Ethanol (96 %) was employed as a solvent for hydrogenation of TNB. The hydrogenation of TNBA was carried out in an aqueous solution or in a mixture of acetic anhydride and acetic acid. The aqueous solution was prepared by suspending a dry TNBA powder in a specified volume of distilled water with the addition of a stoichiometric amount of sodium bicarbonate.

The catalyst was represented by the 6 % Pd/C sample, which was synthesized by the hydrolytic precipitation of palladium polyhydroxo complexes on the surface of carbon material Sibunit and the reduction of the complexes with sodium formate [10]. Moisture content of the catalyst was about 50 %.

The catalytic hydrogenation at atmospheric pressure was performed in a setup consisting of a glass thermostatted reactor, a system for measuring of hydrogen consumption, and a vacuum unit. Mixing was carried out with a magnetic stirrer. Catalytic hydrogenation at elevated pressure was conducted in a 180 mL steel autoclave equipped with a controllable valve for hydrogen input, a sampler, and an external thermostatted jacket.

The reaction products were examined by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, IR spectroscopy and elemental analysis. NMR spectra were recorded on an Avance-400 (Bruker) spectrometer using standard ampoules with the diameter of 5 mm at a Larmor frequency of 400 MHz ( $^1\text{H}$  NMR) or 100.6 MHz ( $^{13}\text{C}$  NMR) at a temperature of 25 °C in a pulsed mode. Acetone- $d_6$  was used as the lock signal. Tetramethylsilane served as the external standard. The IR transmission spectrum was recorded on an IR Prestige-21 (Shimadzu) instrument in the region of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The elemental composition of the product of TNB complete reduction was determined using a universal elemental analyzer Vario EL cube (Elementar Analysensysteme GmbH).

## 3. Results and discussion

### 3.1. Hydrogenation of TNBA at atmospheric pressure

TNBA was hydrogenated at atmospheric pressure as the sodium salt in an aqueous solution and in a medium of acidifying agent (mixture of acetic anhydride and acetic acid). The amounts of TNBA and sodium bicarbonate (for hydrogenation of sodium salt in an aqueous solution) were calculated from the stoichiometric consumption of 100 mL hydrogen (normal conditions) according to the equation of reaction (1). The reaction was run at a temperature of 50 °C, and the substrate to catalyst weight ratio was equal to 6 in all the experiments at atmospheric pressure.

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