

# Highly selective reduction of nitroarenes by *sc*-isopropanol in the presence of zirconia in a flow reactor

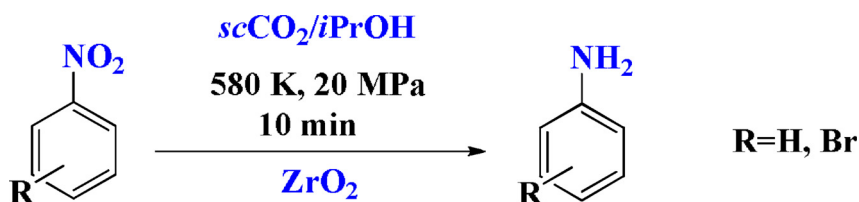
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Reduction of nitroarenes using supercritical isopropanol as a source of hydrogen was studied in a flow reactor in the presence of zirconia at temperatures of 515 – 630 K and with residence time about 10 min. Zirconia was shown for the first time to be an effective and selective catalyst for transfer hydrogenation of nitroarenes. The use of complex supercritical fluid *i*PrOH/CO<sub>2</sub> provided 100% selectivity for aniline at 95% conversion of nitrobenzene. In the absence of CO<sub>2</sub>, the selectivity was reduced due to formation of alkoxylation and *N*-alkylation by-products. The system can also be used for highly selective reduction of bromonitrobenzene avoiding undesired hydrodehalogenation.

## 1. Introduction

The main way to produce aromatic amines that are extensively used in fabrication of polymers, pesticides, dyes, and pharmaceuticals [1,2] is reduction of appropriate aromatic nitro compounds [3]. However, selective reduction of nitro groups in aromatic compounds having other functional groups, e.g., halogen atoms [4,5], is a serious problem. In addition, hydrogenation uses explosive hydrogen at high pressures, which requires special pressure vessels and is associated with safety issues. In recent years, considerable attention has been focused on transfer hydrogenations of nitroarenes using alcohols, hydrazine or

trichlorosilane as a hydrogen source, which is considered as a safe and selective alternative to traditional catalytic hydrogenations [6–12].

Recently, we have found that the use of supercritical isopropanol as a source of hydrogen enables efficient reduction of nitroarenes in a flow-type reactor in the presence of alumina at a short contact time [13–15]. In the reaction isopropanol was converted into acetone. Under these conditions, aliphatic nitrocompounds undergo more complex transformations, in particular unique shortening of the aliphatic chain [16,17]. This system can be successfully applied for reduction of polynitroarenes [14] and halogenated nitrobenzenes [13], but in the case of unsubstituted nitrobenzene, only moderate selectivity is reached

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due to side processes, such as amine group alkylation, aromatic ring alkoxylation, or their combination [13].

Zirconium-based catalysts can be used for transfer hydrogenation of carbonyl compounds in flow-type reactors [18–21]. The purpose of this study is to elucidate the replacement of alumina with zirconia as a catalyst for transfer hydrogenations of nitroarenes to amines would enhance the reaction selectivity in the described system [13].

## 2. Experimental

### 2.1. Materials

Commercially available nitroarenes (Aldrich) were used as received without purification. The supplied isopropyl alcohol contained no less than 99.8 wt. % of the main substance. CO<sub>2</sub> was a stated purity of 99.9 vol. %.

As a starting compound for preparation ZrO<sub>2</sub>, commercial product Zr(NO<sub>3</sub>)<sub>2</sub> of a high purity grade was used. Freshly prepared 1.5 M solution was aged for 15 h at room temperature. Hydrolysis of solution was carried out at nearly constant pH value ~9.5 by rapidly adding it to the aqueous ammonia solution under intensive stirring. Obtained sol was subjected to HTT (Hydrothermal treatment) in the mother liquor in an autoclave first for 24 h at 90 °C and then 110 °C for 8 h. After cooling suspension and filtering precipitate, the obtained product was washed by 0.1 M solution of NH<sub>4</sub>OH and dried at 110 °C, followed by calcination at 750 °C for 4 h. Volume and specific surface area of micropores and mesopores were determined from adsorption isotherms of nitrogen recorded at 77 K using the ASAP-2400 Micrometric instrument. Catalyst structure was characterized by X-ray diffraction (Bruker D8 Advance diffractometer).

### 2.2. Apparatus

Experimental studies were performed in the laboratory-scale set-up described earlier [22,23] (Fig. 1), using a tubular flow-type reactor 1 (6.0 × 0.8 mm, length 3.0 m) loaded with 56 cm<sup>3</sup> (65.7 g) of the catalyst. The initial mixture was fed to a reactor 1 located in a fluidized sand bed furnace 2 through a mixer 3 by two flows. The first flow (CO<sub>2</sub> or isopropanol) was supplied by a syringe pump 4 at a rate of 3.5 ml/min through a heater 5, which preheated it to the reaction temperature. The second flow, substrate solution 6 in isopropanol, was supplied to the mixer 3 by a piston pump 7 at a rate of 2.0 ml/min. The reactor effluent mixture was passed through a condenser 8 and cooled to ambient temperature. After passing through a backpressure reducer 9, the products were collected in a container 10.

The residence time ( $\tau$ ) was ~10 min and was determined as the ratio between the catalyst volume in the reactor  $V_c$  (cm<sup>3</sup>) and the total inlet rate of the mixture  $Q$  (cm<sup>3</sup>/s).

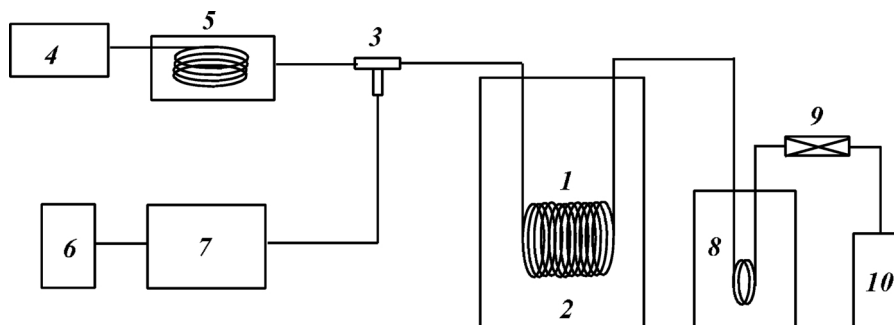


Fig. 1. Experimental setup: 1 – tubular catalytic reactor; 2 – fluidized sand bed furnace; 3 – mixing valve; 4 – syringe pump; 5 – heater; 6 – reagent (1% solution in isopropanol) container; 7 – piston pump; 8 – condenser; 9 – backpressure reducer; 10 – product container.

### 2.3. Experiments

To determine critical parameters of the studied systems and experimental conditions (temperature and pressure) providing single-phase supercritical state of the reaction mixture, thermodynamic calculations and phase diagram plotting were made using RKS EOS [24]. The critical parameters of isopropanol are as follows:  $T_{crit} = 510$  K and  $P_{crit} = 4.7$  MPa [25]. The calculated critical parameters for CO<sub>2</sub>/isopropanol mixture with 80% molar fraction of isopropanol are as follows:  $T_{crit} = 398$  K and  $P_{crit} = 14$  MPa [13]. As we have shown earlier, the effect of nitrobenzene 1, its derivatives and reaction products at the specified concentrations had a negligible effect on the calculated critical parameters of the mixture [13]. The reactions were performed in the temperature interval of 515–630 K at pressure  $P \approx 20$  MPa which were higher than the critical parameters of the mixtures. Moreover, choosing the conditions we took into account the ability to compare new results with the data obtained earlier on Al<sub>2</sub>O<sub>3</sub>, where similar conditions were used [13,14].

The reaction products were cooled at the reactor outlet, separated into gas and liquid phases, and analyzed. Composition of the reaction products in the liquid phase was determined by gas chromatography-mass spectrometry (GC–MS) using an Agilent 7890 A gas chromatograph equipped with a quadrupole mass spectrometer Agilent 5975C as a detector. Quartz column HP-5MS (copolymer 5%–diphenyl–95%–dimethylsiloxane) of length 30 m, internal diameter 0.25 mm and stationary phase film thickness 0.25  $\mu$ m was used for the analysis. The standard deviation for chromatographic analysis is not more than 3%.

Qualitative analysis was performed by comparing retention indices of components and their complete mass spectra with the corresponding data for pure compounds if any and with the data of the NIST library, the Wiley7 library of mass-spectrometric data. The percentage composition of mixtures was calculated from the surface areas of chromatographic peaks using no correction coefficients.

## 3. Results and discussion

### 3.1. Reduction of nitrobenzene

Previously, reduction of nitrobenzene 1 by supercritical isopropanol in the presence of Al<sub>2</sub>O<sub>3</sub> in a flow-type reactor was shown to give aniline 2 as the main product with selectivity of up to 70% [13] (Scheme 1). Under these conditions, the main side process was aromatic ring alkoxylation followed by *N*-alkylation, leading to the formation of products 3 and 4. The addition of another component, *sc*-CO<sub>2</sub>, to the reaction mixture drastically reduced the yield of alkoxylation products 3 and 4, but significantly increased the content of an alkylation product, *N*-isopropylaniline 5 and its unsaturated precursor 6 [13].

In this study, we for the first time demonstrated that ZrO<sub>2</sub> can be used for nitrobenzene 1 reduction by supercritical isopropanol to aniline 2 instead of Al<sub>2</sub>O<sub>3</sub>. ZrO<sub>2</sub> of monoclinic structure with particle size

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