

Research paper

In search of efficient catalysts and appropriate reaction conditions for gas phase nitration of benzene

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Abstract

The present paper is dedicated to the development of a method for the nitrobenzene production using solid acid catalysts, as an alternative to industrial nitration, based on a mixture of concentrated acids. The influence of key parameters of the nitration process (temperature, reagent flow rate, nitrating agent concentration etc.) on the conversion of the initial substrate, the degree of decomposition of nitric acid and the quantity of resulting oxygenates was studied. Recommendations for the selection of effective catalytic systems (high content of Brønsted acid sites with $H_0 < -4$, high specific surface and resistance to HNO_3) were developed and the best conditions for process reactions (temperature 200 °C, aqueous solution of nitric acid with concentration of 30 wt%, “nitric acid:benzene” ratio = 0.76) were found. A method for regeneration of the catalytic activity without unloading the catalyst was proposed. As an example, MoO_3/SiO_2 sample was tested in a dual-mode nitration/regeneration process, which allowed us to increase the flow rates of reagents and obtain catalyst efficiency of up to $STY = 4.09 \text{ g}/(\text{g}_{\text{cat}} \cdot \text{h})$. Several of the most promising catalysts (MoO_3/SiO_2 , WO_3/ZrO_2 and Nafion/support composite) for the process were tested in identical conditions.

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1. Introduction

Nitrobenzene is known to be a key intermediate for the production of aniline (97% of the total production) and benzidine, which are precursors of dyes, drugs and fragrances. Nowadays, the industrial synthesis of nitrobenzene overpasses 5,000,000 tons per year. It consists of the nitration of benzene in liquid phase, using a mixture of concentrated nitric and sulphuric acids [1]. While nitric acid in the mix acts as the main nitration agent, the sulphuric acid protonates the HNO_3 molecule, leading to the generation of active electrophilic species of nitronium cation, which attacks the aromatic ring [2]. Furthermore, sulphuric acid bonds with water, resulting from the nitration reaction, thus ensuring that practically all of the nitric acid is used for nitration. It should be noted that sulphuric acid is not depleted in the reaction, but being deactivated by reaction water

requires regeneration, which is performed by removing water. This step demands considerable energy consumption and is prone to environmental problems [1]. This energy consumption can be reduced to a minimum if an adiabatic process is used, where the heat, released by nitration, is used for the dehydration of the processed sulphuric acid [3]. However, the increase in temperature required for this reaction, as well as the mass-transfer conditions which, in comparison with a batch-reactor, is less favorable, tends to lead to an undesired side oxidation reaction and the formation of nitrophenols, the removal of which requires a multi-stage ablation of the obtained nitrobenzene.

As an alternative to nitration, based on an acid mix, nitroaromatic compounds, primarily nitrobenzene, can also be obtained using solid acid catalysts (Fig. 1). The exclusion of a high turnover of sulphuric acid (the development of more eco-friendly process) and the increased selectivity of the process (mono-substituted compound only is produced) used in this method offer considerable economic advantages. Over the recent years, numerous publications were dedicated to nitration processes using heterogeneous catalysts, such as gas–solid (gas

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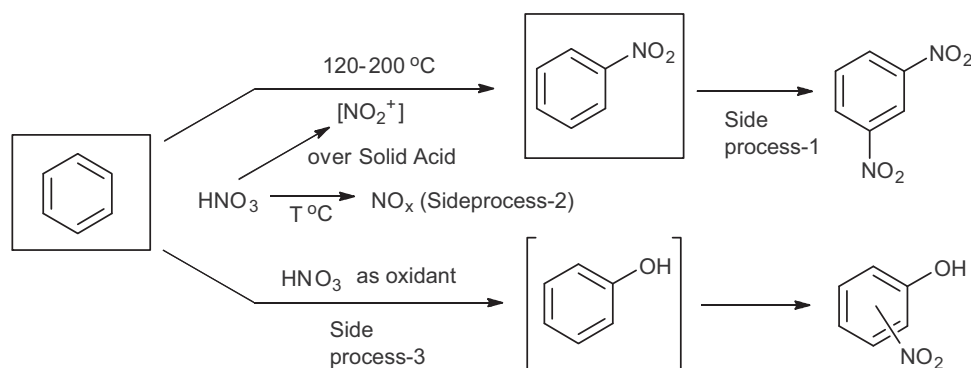


Fig. 1. Scheme of heterogeneous catalytic nitration over solid acids.

phase nitration) and liquid–solid (liquid phase nitration) systems [1,4,5]. Nitric acid [6–24], nitrogen dioxide [25–28] and nitrates decomposed by acid catalysis [29,30] were all used as nitrating agents. Where the process was based on a liquid–solid process (liquid phase heterogeneous catalytic nitration), where nitric acid was used as the nitrating agent, the main disadvantage was found to be the necessity to use an additional process for separation, or binding of the water resulting from the nitration. In many cases, this was resolved by placing the process in an acetic anhydride media (Menke conditions) [31,32], or by using chlorohydrocarbon solvents (dichloroethane, dichloromethane) to remove water by evaporation of an azeotropic mixture [33,34]. These methods, as well as nitration with nitric salts, are useful only where synthesis of a limited amount of nitrogen compounds is required.

An important advantage offered by gas phase nitration of aromatic compounds is the elimination of the phase of separation of the reaction product from the mixture catalyst, as well as a considerable increase in selectivity in the formation of a monosubstituted nitration product. The reaction tested in the present project is the gas phase nitration of aromatic compounds, using the azeotropic solution of nitric acid. This method is the most promising for the production of benzene with a boiling temperature of less than 200 °C. The use of nitric oxides as nitrating agents, allowing the continuous realization of the process (for example, Kyodai nitration process), imposes a considerable increase in the complexity of the reaction system setup [25]. Furthermore, NO_x are considerably less reactive, with inert nitrogen oxide (I) as a side product. The fact that cheap, azeotropic nitric acid is used as the nitrating agent in the search for effective and stable catalytic nitration systems opens the perspective of process industrialization for this method.

So far, the following catalytic systems have been used in gas phase nitration: zeolites and clays, including modified ones (montmorillonite, mordenite, ZSM-5 etc.) [6–10], deposition of acids on SiO₂, mainly H₂SO₄ [11–16,31,32], mixed oxides (Ti, W, Zr, Nb etc.) [17–22,25,26,33,34] and heteropolyacids (phosphor-tungsten, phosphor-molybdenum etc.) [12,28]. Some cases, involving the use of a sulphonated polyorganosiloxane (SPOS) [27] and composite based on sulphated perfluorinated polymer Nafion [23,24] for nitration, have been described. One common feature of these catalytic systems is their high acidity. It

should be noted that the conditions in which the comparison of catalyst features was conducted were not identical. This made the comparative analysis and the selection of the most effective catalytic system difficult. The purpose of the present paper is to analyze the influence of the conditions in which reaction is conducted on the organization of the nitration process and the stability of the catalyst, as well as to test a range of promising oxidation systems and composites, based on a sulphated perfluorinated polymer, in an identical reaction conditions.

2. Materials and methods

2.1. Catalysts

The systems used in our work were the H-ZSM-5 (BIC), composite SAC13 (Nafion/silica, 15 wt%, DuPont). Binary oxides MoO₃/SiO₂ or WO₃/SiO₂ synthesized by sol–gel/coprecipitation of heptamolybdate or ammonium metatungstate (Fluka) with tetraethoxysilane (Aldrich) in *i*-PrOH (with NH₄OH, 2.5% as precipitator), with subsequent calcination of obtained gels at 500 °C [22,34]. In the case of WO₃/ZrO₂, mutual precipitation of ammonium metatungstate and zirconyl chloride (Vekton) with ammonium hydroxide was used, with subsequent annealing at 400 °C [19]. The synthesis of systems H₂SO₄/SiO₂, H₂SO₄/Al₂O₃ and SO₃/ZrO₂ was done by impregnating of the SBA-15, γ-Al₂O₃ supports and the amorphous phase of zirconium hydroxide ZrO(OH), obtained by hydrolysis of ZrOCl₂ with the estimated quantity of sulphuric acid solution (30%) and drying at 120 °C [15,35] (and 300 °C for zirconium oxyhydroxide [36]). Carbonized sulphated naphthalene (CH_{0.35}O_{0.35}S_{0.14}) was synthesized by annealing of the naphthalene mixture and sulphuric acid in the flow of inert gas (N₂) at a temperature of 150 °C [37]. The sulfonation of carbon nanofibers (the CNF, obtained by the decomposition of hydrocarbons over Ni–Cu/Al₂O₃ catalysts [38]) was achieved by heating 2 g of CNF samples in 20 mL of fuming sulphuric acid (120%) at 200 °C. The synthesis of Nafion/silica composite was achieved by precipitation of tetraethoxysilane by sodium hydroxide in the presence of a sulphated perfluorinated polymer Nafion (10 wt%, solution in a mixture of low-molecular alcohols), with the subsequent transfer of the composite into H-form (two-stage washing by 4M HCl composite at 70 °C) [39]. In the case of Nafion/CNF, CNF was impregnated by

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