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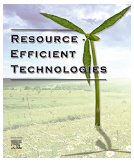

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Research paper

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 $H_o < -4$, 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 $STY = 4.09$ g/($g_{cat} \cdot$ 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.

Keywords: Benzene; Nitration; Catalysts; Conditions; Regeneration

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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 ablution 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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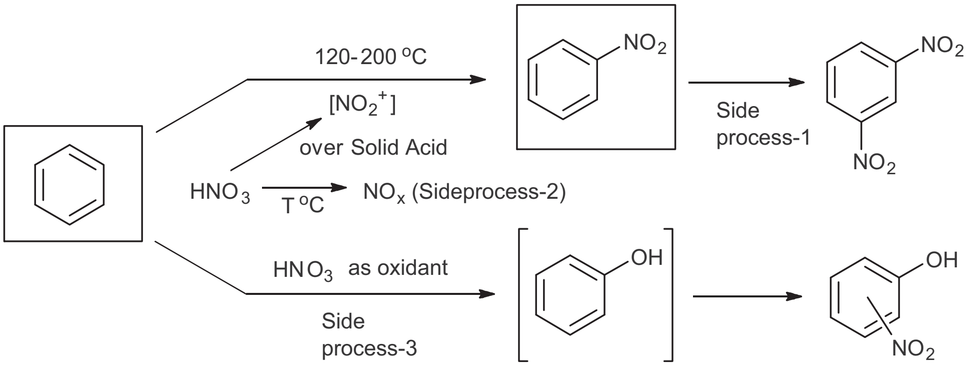

Fig. 1. Scheme of heterogeneous catalytic nitration over solid acids.

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 SiO_2, mainly H_2SO_4 [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 MoO_3/SiO_2 or WO_3/SiO_2 synthesized by sol–gel/co-precipitation of heptamolybdate or ammonium metatungstate (Fluka) with tetraethoxysilane (Aldrich) in i-PrOH (with NH_4OH, 2.5% as precipitator), with subsequent calcination of obtained gels at 500 °C [22,34]. In the case of WO_3/ZrO_2, 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 H_2SO_4/SiO_2, H_2SO_4/Al_2O_3 and SO_3/ZrO_2 was done by impregnating of the SBA-15, γ-Al_2O_3 supports and the amorphous phase of zirconium hydroxide ZrO(OH), obtained by hydrolysis of $ZrOCl_2$ 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 (N_2) at a temperature of 150 °C [37]. The sulfonation of carbon nanofibers (the CNF, obtained by the decomposition of hydrocarbons over Ni—Cu/Al_2O_3 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 tetraetoxyslane 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

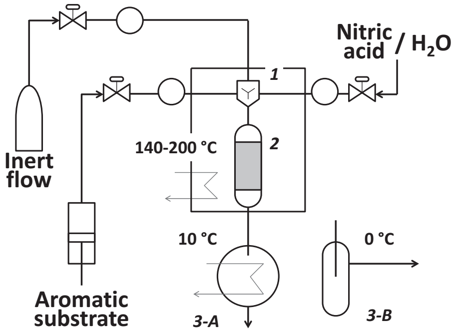

Fig. 2. Scheme of experimental set-up for gas phase nitration of aromatic compounds.

perfluorinated polymer solution, based on absorption volume [24].

2.2. *Characterization of the catalysts*

The overall concentration of acid sites was determined using the back titration method, according to Ref. [40]. The presence of superacid sites ($H_0 < -11.35$) in the sample was evaluated based on adsorption of nitroaromatic compounds (Hammett indicators) by the catalyst surface, according to Ref. [23]. The formation of indicator coloring was recorded with spectrophotometry (400–600 nm). Specific surface (S_{BET}, m^2/g) of synthesized samples was determined using the low-temperature nitrogen adsorption method (Micrometrics ASAP–2400). The elemental analysis of sulphur for Nafion/support and sulphated carbon samples was conducted using the CHNS-O analysis system (Vario EC, Elementar Analysensysteme GmbH).

2.3. *Testing of catalytic activity*

The catalytic activity of the samples was studied using benzene (99.9%), and 30 wt% and 68 wt% aqueous solutions of nitric acid. The aromatic compound gas phase nitration reactor consisted of three subsequently connected sections (see Fig. 2):

1. Evaporation (140–200 °C) and substrate flow mixing system, equipped with liquid lines (aromatic substrate, nitric acid and water) as well as an inert gas line (nitrogen, 10–80 mL/min). The introduction of substrates in liquid lines is conducted using infusion pumps, with a flow rate of (for standard experiments): benzene $WHSV_B = 1.42\ g/(g_{cat} \cdot h)$, nitric acid $WHSV_{NA} = 0.87\ g/(g_{cat} \cdot h)$. Working pressure in reactor was near 1.2 atm. The ratio of aromatic substrate flow to inert flow was varied in a range from 1:2 to 1:8.
2. Thermostat controlled (140–220 °C) flow reactor (Pyrex glass; length 10 cm, inner diameter 8 mm) with a catalyst loading of 1–5 g (0.25–0.5, 0.5–1 or 1–1.5 mm fraction).
3. Reaction mixture condensation section.

In the first case (method A): the gas flow of the reaction mixture was passed through cooling NaOH solution. The resulting organic layer was separated and dried ($MgSO_4$). The conversion of benzene was analyzed by gas chromatography (Crystal-2000M), calculating the STY parameter as X_B*$WHSV_B$/t, $g_{NB}/g_{cat} \cdot h$ (where X_B is the benzene conversion; $WHSV_B$ is the weight hour space velocity of benzene, assigned to catalysts mass; t is the time) and nitrobenzene yield $Y_{NB} = X_B * WHSV_B * \mu_{NA} / (WHSV_{NA} * \mu_B)$, % (where μ_{NA}, μ_B is the molar mass of nitric acid and benzene, and $WHSV_{NA}$ is the weight hour space velocity of nitric acid assigned to catalyst mass). The admixture content was analyzed using the high performance liquid chromatography (HPLC) method, according to Ref. [15]. The conversion of nitric acid (X_{NA}) was assessed by back titration a partially neutralized alkali solution. The selectivity of nitric acid decomposition (side process, S_{NO}) was determined based on nitric acid conversion X_{NA} and benzene conversion X_B differences.

In the second case (method B), the products were condensed in a cooler (10 °C). The condensed reaction mixture was parted and analyzed in a similar manner. Furthermore, the measurement was carried out based on the definition of benzene conversion (X_B) based on the density of the organic phase (d_{op}). In order to assess the selectivity of the nitration process (the amount of nitrophenols and dinitrobenzene in the reaction mixture), method B for the composition of mixture was preferred, due to nitrophenol by-products being transferred to water phase when forming salts. To determine X_B based on density, method A was preferred since the organic phase can be mixed with nitric acid (up to 5 wt% HNO_3 [41]).

2.4. *Regeneration of deactivated catalysts*

For the regeneration of catalysts in the gas phase nitration of benzene, the catalytic layer was purged with a benzene/water/inert gas–mixture ($WHSV_B = 2\ g/g_{cat} \cdot h$; $WHSV_{aq} = 1\ g/g_{cat} \cdot h$) at a temperature of 180 °C.

3. Results and discussion

3.1. *Gas phase nitration of benzene: deactivation and regeneration of the catalysts*

The choice of binary oxide catalytic systems MoO_3/support, WO_3/support to be used in the study of gas phase nitration, was based on all high catalytic features of these materials [19], as well as their stability in a nitric acid media. The interests for the involved materials with chemically bonded sulphate groups (Nafion/support, sulphated carbonaceous materials) are due to the high activity of samples of H_2SO_4/SiO_2 in the initial stages of nitration. Nafion/support samples, having high concentrations of sulfonic acid groups, exhibit a considerably higher resistance to leaching of sulphuric acid from the support surface.

Immediately before the nitration stage, the catalyst was activated, either by a flow of inert gas at a temperature of 160 °C or by running nitric acid through the catalyst layer (transferring solid acid to the H-form). Reducing the average size of catalyst grain leads to an increase in substrate conversion (Fig. 3). A granule fraction of 0.25–0.5 mm was used in standard activity tests. Where smaller dimension catalyst granules were used, the resistance of the catalyst layer to gas flow considerably increased.

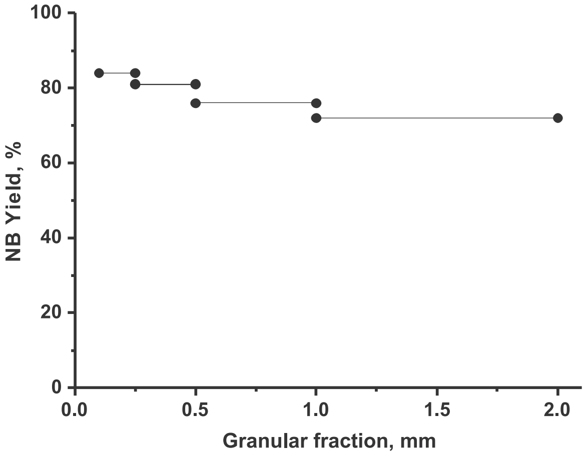

Fig. 3. Dependence of nitrobenzene yield from the granular fraction of MoO_3/SiO_2 catalyst.

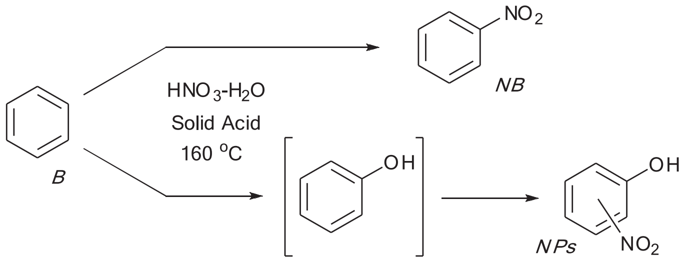

Fig. 4. Scheme of competitive processes of nitration and oxidation of the aromatic substrate.

In order to accelerate the analysis, involving a large amount of reaction mixtures, a substrate conversion determination method was developed, based on the density of an organic phase (OP). The method embraces selecting and weighing (±0.001 g) of an OP aliquot (±0.01 mL) in normal conditions (20 ± 0.1 °C, 1 atm). Benzene conversion was determined based on a predetermined calibrating curve ($X_B = f(d_{of})$). In the calibrating experiments a series of pure nitrobenzene (99.9%) and benzene (99.9%) solutions was used. Obtained solutions were analyzed, based on their density and by gas chromatography. The discrepancy between the two methods did not exceed 1.8%. The measured dependence of the substance density on nitrobenzene's mole fraction does not imply additive character, remaining between 0.75 and 0.8 m.f. of nitrobenzene. Divergence between mixture density and the linear dependence ($d_{mix}(x) = xd_{C_6H_6} + (1-x)d_{C_6H_5NO_2}$) is explained by the change in the packing of molecules within the liquid structure. According to estimated data, the packing of molecules in similar solutions is "stacked", rather than the "T-shaped" packing found in pure mixtures [42]. The obtaining empirical equation $X_B = -1.072 - 0.160d + 1.538d^2$ was used to estimate the benzene conversion in the real reaction mixtures.

With the exception of a few cases involving irreversible catalyst deactivation (leaching of acid sites from a support surface, in the case of H_2SO_4/SiO_2 systems, partial dissolution of the support in the reaction mixture, as in the case of H_2SO_4/Al_2O_3 system, and the support's oxidation in the case of sulphated carbons), the loss of activity could be reversed by regeneration, obtained as a result of the blocking of acid sites by nitrobenzene, formed by the reaction. The slowing down of the targeted nitric acid protonation process tends to lead to deactivation of the catalyst, due to the acceleration of concurrent oxidation processes (Fig. 4) and the formation of high boiling nitrophenols.

Based on several studies, conditions could be selected, to allow the hard-to-desorb molecules to be effectively washed off during the process, extending the life of the catalyst up to 200–300 h TOS [17]. However, this was achieved by increasing the amount of inert gas in the benzene–HNO_3–inert mixture, considerably lowering catalyst efficiency (STY), as the key parameter in the flow process.

It proved more effective to conduct the flow process in two stages, where the nitration phase was followed by the catalyst regeneration phase. To achieve it, pure benzene and water vapors were passed through the catalyst layer at high temperature (180 °C). When durability experiments were conducted, aromatic substrate nitration phases (5 h) were followed by catalyst regeneration phases (30 min). The use of a catalyst regeneration method, without unloading the catalyst, allowed us to increase the flow rate of benzene and nitric acid up to 4.26 g/($g_{cat} \cdot h$) and 2.61 g/($g_{cat} \cdot h$) respectively, as well as obtain catalyst efficiency of STY = 4.09 g/($g_{cat} \cdot h$) in average. It should be noted that when the regeneration procedure was not applied the catalyst efficiency did not exceed 1.4 g/($g_{cat} \cdot h$) even at standard flow rates of reagents (1.42 g/($g_{cat} \cdot h$) for benzene and 0.87 g/($g_{cat} \cdot h$) for nitric acid), and significantly fell down with it increase.

In fact, full regeneration of the deactivated catalyst was obtained using the *ex situ* method: unloading of the catalyst, extraction of by-products (boiling in benzene for 1 h) and calcination at 200 °C on air (1 h). According to HPLC results, the benzene/water solution used for flushing, following *in situ* and *ex situ* methods, consisted mainly of nitrobenzene, with the overall content of nitrobenzene and nitrophenols of <1%.

3.2. Mechanism of heterogeneous catalytic nitration reaction

The nitration reaction occurs on a solid acid surface. The first phase consists of adsorption of substrates from the gas phase and the formation of a nitronium ion with the separation of water. In order for NO_2^+ to be effectively formed on the surface, a large number of acid sites is required ($H_o < -3$) [11].

The existence of a nitronium ion on the surface of the acid catalyst was confirmed on several occasions [43]. However, the mechanism of its formation is subject to debate. The prevailing concept indicates that the decomposition of nitric acid occurs either on Bronsted acid (BAS) or on a Lewis acid sites (LAS) with a water polarization stage. On the other hand, there are published data [44], suggesting that in the case of liquid phase nitration, the decomposition of nitric acid can also occur on sites of a non-acidic nature. In gas phase nitration, Ref. [22] assumes a possibility of the use of oxidation/reduction processes Mo^{5+}/Mo^{6+} when NO_2^+ are formed from nitric acid, with

Table 1
Comparison of the catalytic activity of the studied catalysts depending on strength and concentration of acid sites.

Catalyst	Activity, Y_{NB}, %	Acidity, mmol/g		Surface area, S_{BET}, m²/g
		Weak-medium, mmol/g	High	
H-ZSM-5	37*	0.79	+	394
H_2SO_4/SiO_2 (15%)	56*	1.50	−	210
MoO_3/SiO_2 (20%)	53	1.10	−	180
WO_3/SiO_2 (20%)	50	1.05	+	179
Sulfated CNF	17*	0.27	−	318
Nf/SiO_2 (15%)	42	0.181	−	201
Nf/CNF-318 (15%)	41	0.181	−	140

Reaction conditions: T = 160 °C, WHSV = 1.42 $g/g_{cat} \cdot h$, NA/B = 0.76, TOS = 1 h, inert flow 60 mL/min.
* Rapid deactivation.

a simultaneous operation of two mechanisms. However, most principles observed in published works and in the present study can be explained by acid catalysis concepts. The second stage is based on an interaction between the adsorbed benzene molecule and NO_2^+/A^- ion pair. The mechanism of this phase is also subject to discussion (single-electron transfer mechanism or σ-complex formation mechanism [45]). However, this is not so important, since it leads to the same nitro-products.

3.3. Effect of the acidity and textural characteristics of the catalysts

The analysis indicated that the force of superacid sites of the catalyst does not affect the degree to which nitric acid is decomposed and the produced benzene converted. In spite of the high concentration of superacid sites in the catalytic systems WO_3/SiO_2 and H–ZSM-5, the MoO_3/SiO_2 systems proved more active in nitration, in spite of not containing any superacid sites, at the same time having a larger quantity of medium force acid sites. Another type of a high activity system is the H_2SO_4/SiO_2. However, their activity is quickly reduced due to the leaching of sulphuric groups.

The results of these experiments can be explained by the fact that regardless the strength of superacid sites of the solid acid used these sites are subjected to poisoning by nitric acid to $H_o \sim -4$. In order to test catalytic activity of synthesized systems the gas phase nitration was conducted in identical conditions, at a high flow rate of inter gas (Table 1).

The concentration of catalyst acid sites has considerable impact on the kinetic features of the process. When using catalysts with a low concentration of acid sites (5 wt% Nafion/CNF) the reaction follows a pseudo-zero order in benzene, consequently limiting the speed of the reaction, due to the decomposition of nitric acid on acid sites (Fig. 5). When samples with a higher content of acid sites were used (10–20 wt% Nafion/CNF), a degree of dependence, close to a second order kinetic equation, was observed. In short nitration reactions (<2 h), the process can be closely described with the equation: $dC_{NB}/dt = kC_{NA} \cdot C_B$.

In the case of binary oxides, an increase of specific surface area leads to higher dispersion of MoO_3 and WO_3, thus increasing the concentration of acidic sites [34]. At the same time, the use of supports with developed surface area in Nafion-based composites provides improved accessibility of SO_3H-groups of sulphated perfluoropolymer [24]. In a range of Nf/CNF-x systems (where x is the S_{BET} of carbon nanofibers, used to synthesize the composite) the increase in the surface area led to a reduction in the amount of oxidation by-products and an increase in benzene conversion (Table 2).

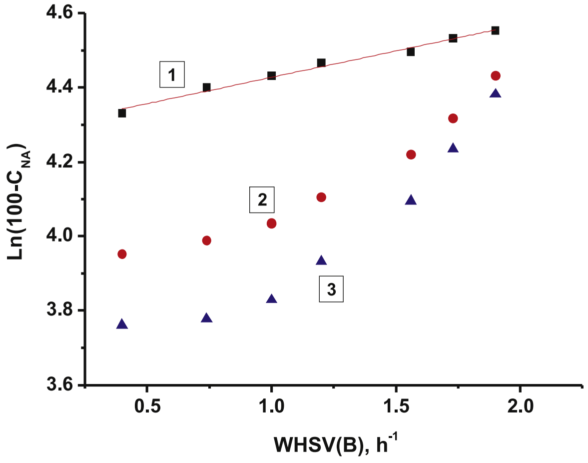

Fig. 5. Concentration of unreacted nitric acid vs. WHSV(B) of benzene for the Nf/CNF-318 catalyst with different Nafion contents: 1–5 wt%; 2–10 wt%; 3–20 wt%.

Furthermore, it was found that the nature of the nitration catalyst has an effect on the speed of aromatic substrate oxidation processes. Consequently, where SO_3/ZrO_2 and WO_3/ZrO_2 oxidizing systems were used, there was an increase in the total quantity of nitrophenols 200–400 ppm, which are typical for catalysts based on more inert supports Nf/SiO_2, Nf/CNF, MoO_3/SiO_2, up to ~550 ppm.

The results described above allows us to conclude that an effective catalyst in gas phase benzene nitration must have the following: a high concentration and accessibility of Brønsted acid sites ($H_o < -3$); high texture characteristics; resistance to the leaching of active sites in a nitric acid environment; an absence of sites promoting oxidation of aromatic substrate.

3.4. Effect of reaction conditions

As already noted in Section 3.1, the quantity of oxidizing products tends to be increased considerably when active sites of the catalyst are blocked. This means that the process of oxidation

Table 2
Relation between stability of the Nf/CNF catalysts and the surface area of CNF.

20 wt.% Nf/CNF-x (x – S_{BET})	Activity, Y_{NB}, % (NP content, ppm)	
	1 h TOS	10 h TOS
Nf/CNF-110	87 (250)	13 (490)
Nf/CNF-140	87 (250)	21 (460)
Nf/CNF-285	89 (230)	67 (300)
Nf/CNF-318	91 (190)	86 (200)

Reaction conditions: T = 160 °C, WHSV = 1.42 $g/g_{cat} \cdot h$, NA/B = 0.76, inert flow 20 mL/min.

Table 3
Effect of temperature and concentration of nitric acid on nitrobenzene yield.

Reaction temp., °C	Nitrobenzene yield (Y_{NB}), % (selectivity of nitric acid decomposition (S_{NO}), %)					
	30 wt% HNO_3			68 wt% HNO_3		
	H_2SO_4/SiO_2	MoO_3/SiO_2	Nf/CNF	H_2SO_4/SiO_2	MoO_3/SiO_2	Nf/CNF
140	54 (1.1)	71 (1.3)	63 (0.7)	71 (2.0)	74	90
160	60	94	94	98	96	91
200	69	95	95	40	36	84
220	71 (3.1)	95 (4.5)	96 (1.5)	39 (10.3)	37 (11.1)	61 (8.3)

Reaction conditions: WHSV = 1.42 $g/g_{cat}/h$, NA/B = 0.76, TOS = 1 h, inert flow 20 mL/min.

of aromatic substrate can be carried out with thermal oxidation by nitric acid. The acceleration of the substrate removing from the oxidizing danger zone of the reactor, as well as the acceleration of desorption of high-boiling nitric products, is bound to have a considerable effect on the process selectivity.

3.4.1. Effect of temperature and concentration of nitric acid

Gas phase nitration of aromatic compounds is known to occur somewhere between the boiling point of the azeotropic nitric acid solution ($T_{boil} = 121$ °C) and the point of thermal stability of nitric acid. When using temperatures of <120 °C there may be some non-uniformity in the flow of nitric acid, due to the difference in concentration of the nitrating agent in the liquid and gas phases (in the case of a non-azeotropic solution). Once the upper limit is crossed, the irreversible process of decomposition of nitric acid starts and less reactive nitric oxides are formed, reducing the selectivity of the process in respect of nitric acid (S_{NO}).

An interesting feature of the gas phase nitration was the lowering of the concentration of by-product compounds and an increased stability of the catalyst when the process temperature was increased. This principle was most noticeable in respect of Nf/support, H_2SO_4/SiO_2 and MoO_3/SiO_2 catalysts (Table 3). An increased temperature facilitates desorption of the products of reaction and accelerates the nitration, as the target reaction. Consequently, in the case of nitration based on 68 wt% nitric acid solution, increasing the temperature of process is useful up to 180 °C, while at higher temperatures processes of oxidation and nitric acid decomposition are being accelerated.

Some works [21,46] were based on gas phase nitration using diluted nitric acid (30 wt%). One important advantage of using diluted nitric acid was the possibility of increasing the maximum reaction temperature for nitration up to 200 °C, whereas the diluted acid shows less oxidative behavior and higher resistance to the decomposition processes (reduction of S_{NO}). In this case, a higher rate of benzene and nitric acid conversion is achieved.

According to our results, this principle is also due to activation of the catalyst with water. While in the case of oxide systems, the activation of the system can be achieved by water polarization on acid sites; systems based on sulphated perfluorinated polymer produce a swelling-effect, leading to the widening of polymer channels and an increase in the accessibility of sulfonic acid groups [47].

3.4.2. Effect of space velocity of the substrates and flow rate of an inert gas

A reduction of weight hour space velocity (WHSV, $g/g_{cat} \cdot h$) of the substrates (and a subsequent increase of contact time) tends to lead to an increase in conversion of the target product. However, the productivity of the catalyst in respect of nitrobenzene (STY_{NB}) is consequently reduced. On the other hand, an increase in the speed of the introduction of substrate and reduction in the inert gas flow (Fig. 6) considerably reduces the time of stable action of the catalyst. The maximum permissible flux of benzene $WHSV_B$ for the solid acid used here can be evaluated from the value of the benzene monolayer volume (V_m, based on the Langmuir adsorption equation $V = V_m K/(1 - K)p_B$). When these values are exceeded, a benzene film is supposedly formed on the catalyst surface, thus blocking its active sites. In the case of H_2SO_4/SiO_2, MoO_3/SiO_2, Nf/CNF-318 systems, the values of $WHSV_{B,max}$ were 5 $g/g_{cat} \cdot h$. With the increase of $WHSV_B$, it was observed that the rate of inert gas flow in a wide range (20–60 mL/min) has practically no effect on the conversion of initial substrate.

The gas phase nitration process is best provided at excess of the benzene. This is due to two factors: firstly, an increased benzene flow leads to an increase in the eluting ability of the flow (removing the products of reaction from the catalyst surface). Secondly, complete transformation of nitric acid, with

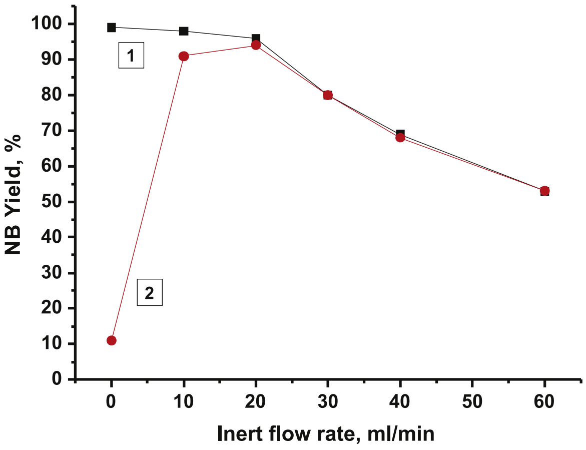

Fig. 6. Effect of flow rate of inert gas on nitrobenzene yield (1–1 h TOS; 2–10 h TOS; reaction conditions: MoO_3/SiO_2, T = 160 °C, WHSV = 1.42 $g/g_{cat} \cdot h$, NA/B = 0.76).

minimum decomposition, is very important for industrial scale implementation of the nitration process. This is due to the necessity of a crude nitrobenzene concentration stage (removal of unreacted benzene). The nitric acid admixture, collected in this way (due to partial solubility of HNO_3 in nitrobenzene), increases the risk of explosion during the process.

The most efficient “nitric acid:benzene” mole ratio for all examined catalytic systems was found to be 0.7–0.8. An increase in this ratio leads to considerable increase of an oxidation process and reduction of selectivity of the nitration process (for example, with a “nitric acid:benzene” ratio of 1, formation of up to 800 ppm of nitrophenol was observed, as well as a high degree of decomposition of nitric acid into nitrogen oxides). Within the optimized reaction conditions, the total amount of by-products does not exceed 0.2 wt% (about 200–350 ppm of 2,4-dinitrophenol and para-nitrophenol, and up to 2000 ppm of dinitrobenzene).

4. Conclusions

As part of this study, samples of solid acid catalysts H-ZSM-5, SAC13, MoO_3/SiO_2, WO_3/SiO_2, WO_3/ZrO_2, SO_3/ZrO_2, $CH_{0.35}O_{0.35}S_{0.14}$, SO_3H-CNF, H_2SO_4/SiO_2, H_2SO_4/Al_2O_3, Nafion/silica, Nafion/CNF were tested in gas phase benzene nitration, using diluted nitric acid (30 and 68 wt%). The influence of key parameters of the nitration process (process temperature, reagent mass-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 $H_o < -4$, a high specific surface and resistance to HNO_3) were developed and the best conditions for process reactions (200 °C, nitric acid concentration 30 wt%, “nitric acid:benzene” ratio = 0.76) were defined. It was shown that regeneration of the catalytic activity without unloading the catalyst leads to an increase of process efficiency up to 4.09 $g/g_{cat} \cdot h$. Several of the most perspective process catalysts were tested in identical conditions: MoO_3/SiO_2, WO_3/ZrO_2 and Nafion/support composite. It was shown that the most promising system is MoO_3/SiO_2.

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