



Toluene and chlorobenzene dinitration over solid $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst

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ABSTRACT

A new catalyst, $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$, was prepared by modification of $\text{MoO}_3/\text{SiO}_2$ using phosphoric acid. The characterization of the catalyst was performed using Infrared and Raman Spectroscopy, potentiometric titration and nitrogen adsorption–desorption methods. Molybdenum oxides were identified along with phosphomolybdic acid and polymolybdates on the modified surface. The suitability of the catalysts for toluene and chlorobenzene nitration in continuous process was examined. Toluene is effectively nitrated to dinitrotoluene (DNT) in one-stage process (96 wt.% of DNT in the product) and in mild conditions i.e. at room temperature and only with ten-fold excess of nitric acid. In chlorobenzene nitration only twelve-fold excess of nitric acid is needed to obtain as high yield as 95 wt.%. Most importantly, the novel catalysts we have developed, provide the opportunity for sulfuric acid- free nitration of aromatic compounds.

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1. Introduction

Nitro aromatic compounds are produced in great amounts for civilian and military uses [1–4]. One of the most common processes in the chemical industry are dinitrotoluene (DNT) and dinitrochlorobenzene (DNCIB) synthesis.

DNT is used in manufacture of polyurethanes (used as e.g. glues, lacquers), which are produced in amount of ca. 10 million tons per year [5]. Furthermore, DNT is an important compound used in the explosive trade as constituent of gun powders, propellants and explosive mixtures [4]. On the other hand, DNCIB is one of the compound that is commonly used in synthesis of explosives [6] and is a starting material in production of 2,4,6-trinitrophenylmethyl nitramine (Tetryl), hexanitrodiphenylamine (HNDP), 2,4,6-trinitrophenol (Picric acid, TNP), trinitroanisole, etc. Furthermore, it is used in manufacture of dyes, e.g. Sulphur Black.

Basically, nitro aromatic compounds synthesis is not an eco-friendly process. DNT and DNCIB are obtained by nitration in the presence of nitric and sulfuric acid mixture [1–6]. Sulfuric acid is relatively effective catalyst in nitration because the reaction yields are high. However, the catalyst cannot be reused and its regeneration process is expensive and onerous. There can be also difficulties in the separation of the products from the reaction mixture, because they are dissolved in the mixture of acids. Furthermore, the nitration mixture is corrosive and dangerous in handling which additionally increases the plant and operating costs. After

nitration there is a great amount of waste in the form of diluted acids and by-products (effect of oxidation or sulfonation). All these disadvantages show that applying the mixture of nitric and sulfuric acid is neither ecological nor economical, despite of relatively low price of sulfuric acid.

A new class of catalysts used in nitration comprises the solid acid catalysts, which have on their surface strong acidic centers. The use of these catalysts in nitration reactions can be advantageous due to the ease of product and catalyst separation from the reaction mixture. They may be characterized by high activity and selectivity in the reactions and their application very often reduces quantities of hazardous waste e.g. diluted sulfuric acid [7,8].

According to the recent literature data, acid strength of the catalysts may be increased by their modification by phosphoric acid. An example is TN nitration over zeolite ZSM-5 modified by phosphoric acid [9,10] whose activity was shown to be higher than activity of unmodified zeolite. Moreover, in nitration with this system, high selectivity to isomer *para*-nitrotoluene was obtained.

Solid acid catalysts prepared by mixing titania and phosphoric acid in the molar ratio of 1:1 and heating at 200–220 °C on a sand bath were also used in nitration [11]. The catalysts were shown to be effective in nitration of various aromatic compounds (e.g. naphthalene, anthracene, phenanthrene) that may be further used as substrates in fine chemicals synthesis.

Furthermore, solid oxide catalysts modified by phosphoric acid or its salts are described in literature [12]. The phosphate-modified $\text{TiO}_2\text{-SiO}_2$ catalyst was found to be an efficient and selective catalyst for solvent-free mononitration of TN.

Other method of catalyst modification by phosphoric ions involves direct synthesis of active domains on the carrier surface.

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As an example, benzene nitration in the presence of a catalyst prepared by heating ammonium molybdate with ammonium orthophosphate can be presented [13]. The catalytic system consisted of ammonium salt of 12-phosphomolybdic acid (HPM, very strong Brønsted acid [14,15]) was effective in mild conditions and the nitration yield and selectivity to nitrobenzene were satisfactory.

Our research is basically devoted to the solid catalyst systems consisted of molybdenum oxide (VI) supported on SiO_2 carrier that are obtained by ammonium molybdate thermal decomposition [16,17]. From our experience, we know that the highest activity in toluene (TN) nitration (i.e. the yield over 90 wt.%) were observed for catalyst containing 15 wt.% of MoO_3 ($\text{MoO}_3/\text{SiO}_2$). In order to improve the catalyst activity (according to described data) we modified the $\text{MoO}_3/\text{SiO}_2$ system by phosphoric acid and investigated its application to nitration of toluene and chlorobenzene (CIB). It was determined that $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst, in which 1 mole of H_3PO_4 is used on 3 moles of MoO_3 , was the most effective in nitration in batch process since substantial amount of DNT (i.e. 15 wt.%) was obtained in TN mononitration (molar substrate ratio TN: HNO_3 is 1:1.5) in mild conditions.

In this work, we continue our studies on nitration with the $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst. The results of TN and CIB nitration under continuous conditions are reported and their impact on making the process more ecological and economical in comparison to the batch process is highlighted.

2. Experimental

2.1. General

Materials taken from POCH Gliwice: toluene (pure), chlorobenzene (pure), fuming nitric acid (pure), ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ (pure), phosphoric acid (85%, pure), sodium hydrogen carbonate (NaHCO_3 , pure), 1,2-dichloroethane (pure), hydrochloric acid (pure). Silica gel (SiO_2) was purchased from Małty, Poland, 12-phosphomolybdic acid (pure) from Sigma Aldrich and *n*-butylamine (pure) from Fluka Analytical.

Analysis of the reaction products was made using gas chromatography with a PerkinElmer Auto System XL and a Rxi-5Sil MS (30 m \times 0.53 mm \times 1.5 μm) column. The sample of post-reaction mixture was dissolved in 1,2-dichloroethane. The quantitative composition of prepared substances were calculated by internal standard method using peak areas and chlorobenzene as internal standard (IS).

Raman spectra were recorded on a Nicolet Almega Dispersive Raman Spectrometer. Infrared spectrum was recorded as KBr pellets on Nicolet 6700 interferometer (4000–400 cm^{-1} , resolution 4 cm^{-1}).

Textural properties of the catalysts surface were determined using a specific surface area analyzer and the microporosity Micromeritics ASAP 2020M. Adsorption/desorption experiments were made for dinitrogen within the p/p_0 range of 0.02–1.0 at -196°C . Specific surface area was determined on the basis of the BET method for p/p_0 range of 0.08–0.30 [18].

The acidity of the catalyst was determined by measurements of initial electrode potential and potentiometric titration method [13,19,20]. Certain 1 g of catalyst was suspended in acetonitrile and the system was magnetically stirred for 1 h. The suspension was titrated with a solution of 0.05 N *n*-butylamine in acetonitrile. Then the variation in the electrode potential was measured with pH meter, using a standard glass electrode. The total number of acidic sites were determined by the amine titration method. The catalyst (500 mg) was suspended in solution of 0.1 N *n*-butylamine in dry toluene and the suspension was left for 24 h. Then 5 mL of solution

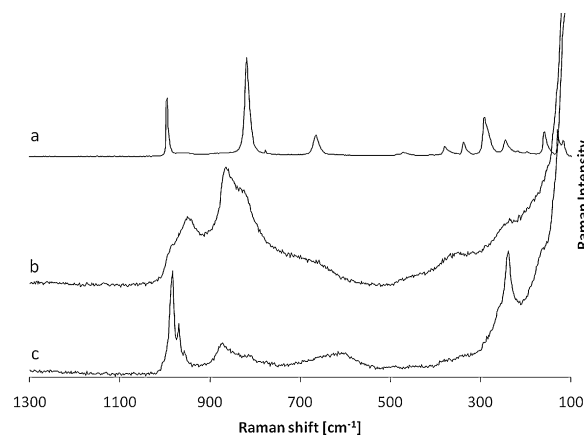


Fig. 1. Raman spectra of main domains present on the $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ surface: a. molybdenum oxide, b. polymolybdates c. phosphomolybdic acid (HPM).

was taken from above of the solid. To this solution 5 mL of distilled water was added and the mixture was titrated with 0.05 N HCl to phenolphthalein.

2.2. Catalysts preparation

To obtain 5 g of the $\text{MoO}_3/\text{SiO}_2$ catalyst, 0.9 g (0.75 mmol) of ammonium molybdate tetrahydrate was dissolved in 7 mL 3% H_2O_2 . The solution of the salt was then applied by wet impregnation method on 4.25 g of SiO_2 (grains 0.6–1 mm). First, the catalyst was dried at 110°C . Next it was heated at 300°C for about 16 h. As a result, 0.75 g (5.2 mmol) of MoO_3 (the oxide constituted 15 wt.% of the catalyst mass) was obtained. Solution of phosphoric acid (1 mol of acid on 3 mol of MoO_3) was applied by wet impregnation onto the catalyst made in the first step. Re-heating was conducted at 300°C for about 16 h.

To obtain 5 g of HPM/SiO_2 catalyst 0.8 g of HPM was dissolved in 7 mL distilled water. Then the solution was applied on 4.2 g of SiO_2 , dried at 110°C and heated at 300°C for 1 h.

2.3. Nitration process

In a flow reactor provided with a cooling jacket the catalysts was placed. Fuming nitric acid and substrate (toluene or chlorobenzene) was fed onto the catalyst bed and the substrate flow was selected to obtain a HNO_3 :toluene molar ratio required. The mixture flow rate was set at ca. 10 mL/h. The post-reaction mixture was washed with aqueous NaHCO_3 and then with water. In toluene nitration the post-reaction mixture contained mononitrotoluenes (MNT): *ortho*-nitrotoluene (*o*-NT), *meta*-nitrotoluene (*m*-NT), *para*-nitrotoluene (*p*-NT) and dinitrotoluenes (DNT): 2,4-DNT, 2,6-DNT and 3,4-DNT. In chlorobenzene nitration the post-reaction mixture contained mononitrochlorobenzene (MNCIB) and dinitrochlorobenzene (DNCIB).

3. Results and discussion

3.1. Catalyst characterization

In order to determine domains obtained on the surface Raman spectra were recorded. Representative spectra of main domains present on the $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ are presented in Fig. 1.

In Fig. 1a the observed bands at 994, 818, 665, 470, 373, 332, 282 and 236 cm^{-1} are characteristic for the crystalline orthorhombic molybdenum oxide (α - MoO_3) [19–22]. During the impregnation by phosphoric acid, a local excess of molybdate concentrations may occur and lead to formation of these crystallites.

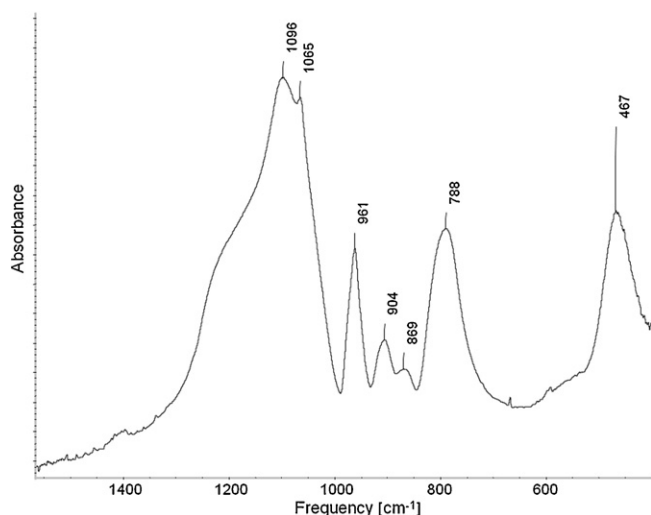


Fig. 2. IR spectrum of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$.

In the spectrum in Fig. 1b broad bands at 800–900 and 900–1000 cm^{-1} are observed. These bands could be attributed to polymeric structures of molybdates with Mo–O groups [23–26]. The polymeric layer is known to be built from MoO_6 octahedra. A broad, weak band at 200 cm^{-1} could be assigned to a deformation mode of Mo–O–Mo groups and indicates the oxygen bridges between molybdenum atoms in polymolybdates.

In addition, the characteristic bands for Keggin structure of phosphomolybdic acid (HPM) are observed in Fig. 1c. The peaks at 990 and 970 cm^{-1} are assigned to the stretching mode ($\nu \text{ Mo-O}_d$) of the terminal Mo=O groups in the molecule of HPM [27,28]. The sharp band at 250 cm^{-1} can be assigned to the stretching mode ($\nu \text{ Mo-O}_a$) between the molybdenum atom and the oxygen atom that links central tetrahedron of each PO_4 to Mo–O octahedron. It is clear that domains of HPM are formed in the reaction of phosphoric acid and molybdate ions, however, all molybdenum compounds do not react with added phosphoric acid (Fig. 1b).

Fig. 2 shows the IR spectrum for the $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst. Bands at ca. 1100, 800 and 470 cm^{-1} can be assigned to SiO_2 [28]. The typical pattern of HPM is therefore partially obscured by the SiO_2 bands. However, a Keggin unit may still be characterized by the $\nu_{\text{as}} \text{ Mo-Ot}$ (t-terminal O atom in Keggin unit) band at about 961 cm^{-1} [28]. This band may confirm that domains of HPM are indeed present on the surface.

Potentiometric titration technique enables the determination of the total number of acidic sites and their strength. The maximum acidic strength of the surface sites may be described by initial electrode potential (E_i) [15,19,20]. E_i amounts 230 mV for SiO_2 , 561 mV for $\text{MoO}_3/\text{SiO}_2$ and increases for catalysts modified by H_3PO_4 to 646 mV. Therefore, the acidic strength of the surface sites increases after addition of phosphoric acid. From the plot shown in Fig. 3, it can be found that titration process of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ requires higher amounts of *n*-butylamine than it is needed for $\text{MoO}_3/\text{SiO}_2$. The total number of acidic sites were determined by *n*-butylamine titration and equals 1.0 mmol g^{-1} for $\text{MoO}_3/\text{SiO}_2$ and 1.2 mmol g^{-1} for $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$. Therefore, it may be concluded that the amount of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ surface acidic centers is higher than amount present on $\text{MoO}_3/\text{SiO}_2$ and SiO_2 .

The results of surface analysis of catalytic systems made by nitrogen desorption–adsorption methods are presented in Table 1. The formation of molybdenum oxide on SiO_2 causes surface area to be reduced by about 30 $\text{m}^2 \text{g}^{-1}$ with respect to the carrier (BET isotherm). Phosphoric acid impregnation on the $\text{MoO}_3/\text{SiO}_2$ brings about a slightly decrease in the surface size compared to

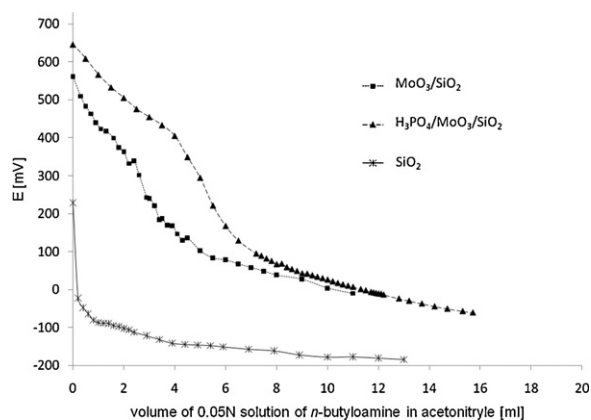


Fig. 3. Potentiometric titration curves of SiO_2 (carrier), $\text{MoO}_3/\text{SiO}_2$ and $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalysts.

$\text{MoO}_3/\text{SiO}_2$. Probably domains of HPA and polymolybdates are responsible for this surface area reduction.

3.2. Toluene nitration

Firstly, toluene nitration in continuous process was carried out with a little excess of nitric acid at 60 °C. The results are presented in Table 2.

The $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst is active in nitration from the beginning. TN conversion is high and amounts ca. 96 wt.%. The utilized amount of nitric acid is not enough to obtain a complete toluene conversion to DNT but is sufficient to obtain 25 wt.% of DNT in the post-reaction mixture. When the reaction is continued, the yield decreases to 70 wt.% and basically stabilizes at this level. It is probably caused by surface active centers blocking by the products that are not totally washed off from the catalyst. This amount of nitric acid is not enough to wash off all the products from catalyst deposit and in the result the products are accumulated. Since reaction yield decreases as a result of centers blocking and the amount of DNT is stable (20 wt.%), it may be concluded that accumulated mononitrotoluenes are nitrated to DNT and then they are washed off.

Toluene nitration was carried out with eight- and ten-fold excess of nitric acid (substrate molar ratios 8:1 and 10:1). A comparison of nitration results are presented in Fig. 4. In both cases almost complete toluene conversion is achieved in mild conditions (room temperature, 5 g of catalyst). Almost 100 wt.% of DNT is obtained with substrate ratio 10:1 and this amount is stable at least for 15 h.

In the reaction carried out with eight-fold excess of HNO_3 an increase of DNT amount is observed along with process time. Therefore, such an amount of nitric acid enables to obtain DNT but is not sufficient to wash off the product from the catalyst deposit. It is the same situation as described above nitration with three-fold excess of nitric acid where the main product was accumulated. Only when next portions of acid are provided, compounds adsorbed on the grains are washed off. However, as it is seen in Fig. 4, ten-fold excess of nitric acid is sufficient to prevent permanent product

Table 1
Textural parameters of SiO_2 , $\text{MoO}_3/\text{SiO}_2$ and $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalysts.

Catalyst	Surface area ($\text{m}^2 \text{g}^{-1}$)		Micropore area ($\text{m}^2 \text{g}^{-1}$)
	BET	Langmuir	t-Plot
SiO_2	279	453	27
$\text{MoO}_3/\text{SiO}_2$	249	405	17
$\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$	245	400	15

Table 2
Toluene nitration in continuous process with substrate molar ratio $\text{HNO}_3:\text{TN} = 3:1$ at 60°C (5 g of catalyst).

Time (h)	TN Conversion (wt.%)	Product composition (wt.%)		DNT composition (wt.%)			2,4/2,6 ratio	MNT composition (wt.%)		
		MNT	DNT	2,4-DNT	2,6-DNT	3,4-DNT		<i>o</i> -NT	<i>m</i> -NT	<i>p</i> -NT
0	95.9	75	25	77.2	18	4.8	4.29	52.1	3.6	44.3
10	70.4	83.3	16.7	75.9	17	7.1	4.46	53.3	3.7	43.3
15	76.9	79.4	20.6	77.3	17.5	5.2	4.42	53.1	3.5	43.3

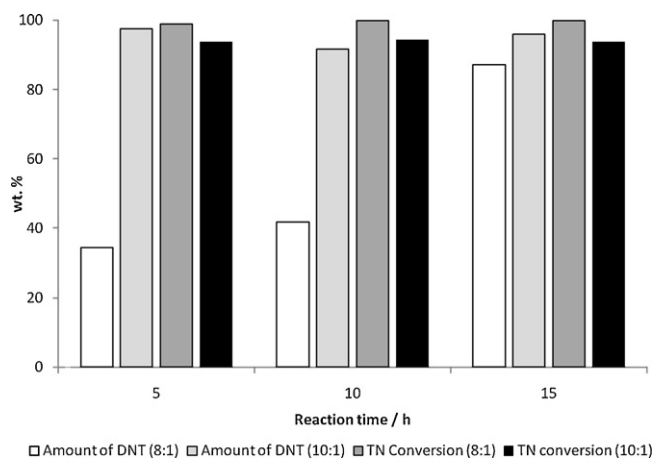


Fig. 4. Toluene nitration in continuous process with $\text{HNO}_3:\text{TN}$ substrate ratio 10:1 and 8:1 (5 g of catalyst, room temperature).

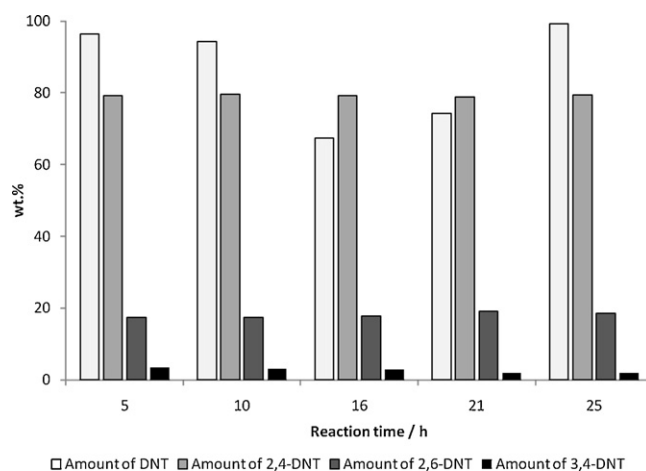


Fig. 5. Toluene nitration in continuous process with substrate molar ratio $\text{HNO}_3:\text{TN} = 8:1$ at 60°C (5 g of catalyst).

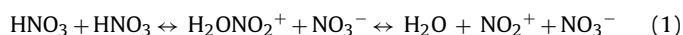
accumulation and DNT is obtained in post-reaction mixture from the beginning.

According to dinitration mechanism [1,2] *o*-NT is nitrated to 2,4-DNT easier than other isomers. Steric barriers that occurs in *o*-NT molecule (spatial methyl group next to nitric group) cause lower amount of 2,6-DNT to be formed from this isomer. 2,4-DNT is formed also in *p*-NT nitration, however, it is also hindered on account of steric barriers. Since 2,6-DNT is not formed from *p*-NT there should be the highest amount of 2,4-DNT in the reaction product. Indeed, in nitration products (Table 3) there is ca. 80 wt.% of 2,4-DNT among DNT and *o*-NT is in the minority among MNT. This product composition is maintained for all reaction times.

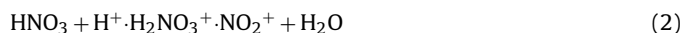
In order to compare the effectiveness of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ and HPM, which is one of the strongest inorganic acid, the continuous process of toluene nitration over HPM supported on SiO_2 (HPM/ SiO_2) was carried out (Table 3). In the latter toluene conversion equals to ca. 100 wt.%, however the amount of DNT is relatively low in comparison to the reaction with $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$. Moreover, this amount decreases along with the process time, which indicates that HPM/ SiO_2 loses its activity. To sum up, the $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ system has similar activity in

toluene nitration to HPM/ SiO_2 , but is more efficient and stable for longer time.

Toluene nitration to DNT occurs only in the presence of nitronium cation (NO_2^+) [1,2]. In the nitration with HNO_3 and $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalytic system in continuous process there are two factors that facilitate NO_2^+ formation i.e.: the excess of nitric acid and the presence of active acidic species on the catalyst surface. Nitronium cation generation in the presence of the excess of nitric acid occurs by acid autoprotection:



However, in the presence of the catalyst NO_2^+ can be also generated in nitric acid protonation by strong protonic acid:



As shown in Section 1, on the surface of the examined catalyst there are domains of HPM, which is a very strong Brønsted acid ($\text{p}K_1 = 2.0$), stronger than nitric acid ($\text{p}K_1 = 9.4$) and sulfuric acid ($\text{p}K_1 = 6.6$) [29]. Therefore HPM is able to protonate nitric acid according to the reaction (2) and it can generate nitronium cation very effectively.

Table 3
The composition of nitration product in the reaction with substrate molar ratio $\text{HNO}_3:\text{TN} = 10:1$ (5 g of catalyst, room temperature).

Time (h)	Amount of DNT (wt.%)	DNT Composition (wt.%)			2,4-/2,6 ratio	Amount of MNT (wt.%)	MNT composition (wt.%)		
		2,4-DNT	2,6-DNT	3,4-DNT			<i>o</i> -NT	<i>m</i> -NT	<i>p</i> -NT
$\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$									
5	97.5	80	18	2	4.44	2.5	24.4	6	69.6
10	91.6	80.5	18	1.5	4.47	8.4	37	3.6	59.4
15	96	81.5	16.9	1.4	4.82	4	7.9	3	89.1
HPM/ SiO_2									
5	81.2	79.9	18.3	1.8	4.37	18.8	44.2	4.3	51.5
10	74.3	80	18.2	1.8	4.39	25.7	48	3.8	48.2
15	57.7	80.5	18.1	1.4	4.43	42.3	50.4	3.1	46.5

Table 4The comparison of reaction yield in batch and continuous process (5 g of catalyst, 2.5 h, room temperature, substrate molar ratio $\text{HNO}_3:\text{TN} = 10:1$).

Type of reaction	Amount of TN (mmol)	TN conversion (wt.%)	Product composition (wt.%)		Amount of DNT (mmol)	Catalyst Activity ($\text{mol}_{\text{TN}} \text{mol}_{\text{Mo}}^{-1} \text{h}^{-1}$)	Space time yield ($\text{g}_{\text{TN}} \text{g}_{\text{kat}}^{-1} \text{h}^{-1}$)
			DNT	MNT			
Batch	4	100	34.6	65.4	1.4	0.31	0.074
Continuous	47.3	93.7	97.5	2.5	43.2	3.32	0.87

Furthermore, molybdenum oxide in the presence of water transforms into polymeric structures of molybdates [16]. The polymolybdates are known to be built of linear chains linked by oxygen atoms Mo–O–Mo. In these structures active Brønsted acid centers may be located on terminal and bridge oxygen atoms where hydrogen cations can be bound. Since polymeric layer covers both the surface and the catalyst pores (as it is manifested in lower surface area of $\text{MoO}_3/\text{SiO}_2$ than SiO_2 , Table 1) it can be expected that there is a relatively great amount of active acidic sites on the surface. In summary, the presence of active acidic centers (domains of HPM and polymolybdates) and excess of nitric acid enable to obtain high nitronium cation concentration in a short time which leads to high-yield nitration of toluene to DNT.

The comparison of the toluene nitration yield in continuous process to the yield in batch process has been also made (Table 4). In batch process with 5 g of catalyst complete toluene conversion is achieved. However, this amount of catalyst is not enough to obtain the same amount of DNT as it is obtained in continuous process. Thirty-fold increase of product amount is obtained in the continuous process in the same time in comparison to batch process. Therefore, nitration in continuous process is significantly more efficient and enables to use the catalyst more effectively (catalyst activity factor is about ten-fold higher than in batch process). Space time yield is order of magnitude higher in continuous process.

Nitration with lower excess of nitric acid (substrate molar ratio $\text{HNO}_3:\text{TN} = 8:1$) was examined at higher temperature (60°C) (Fig. 5). At this temperature also complete TN conversion to DNT is possible. Higher temperature decreases DNT absorption in catalyst pores and then this amount of nitric acid enables to wash off the product from the beginning. After 16 h the amount of DNT decreases from 97 wt.% to 70 wt.%. Therefore, after this time the catalyst was regenerated by phosphoric acid impregnation (the same amount of acid as was used in the preparation) and re-heating at 300°C for 1 h. This operation causes catalyst reactivation probably by HPM domains re-formation, because in the next hours the amount of DNT is increased. The composition of DNT is stable in this conditions, ca. 80% of 2,4-DNT, ca. 17% of 2,6-DNT and ca. 3% of 3,4-DNT are obtained. Therefore, applying higher temperature to the process enables to decrease the amount of nitric acid from 10:1 to 8:1 (substrate molar ratio $\text{HNO}_3:\text{TN}$) retaining the similar yield

and selectivity. The simple regeneration process allows to use the catalyst for a long time.

3.3. Chlorobenzene nitration

Chlorobenzene nitration in continuous process was carried out with various excess of nitric acid in the presence of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst. Chlorine is a functional group attached to a benzene molecule that removes electron density from the benzene ring [30]. This causes deactivation of aromatic ring to electrophilic aromatic substitution reaction. CIB nitration occurs slower and requires more drastic conditions in comparison to TN nitration [1–4,30,31]. Therefore, in CIB nitration greater amounts of nitric acid, longer reaction time and higher temperature are necessary. In Table 5 results of CIB nitration in continuous process in the presence of $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst are presented.

Complete CIB conversion is obtained in the reaction with ten-fold excess of nitric acid. However, after 5 h in these conditions only 27.9 wt.% of DNCIB is formed. In the next 10 h the amount of DNCIB is increased. This suggests accumulation of the product in the catalyst deposit and that ten-fold excess of nitric acid is not enough to wash off the whole product from catalyst. When substrate molar ratio $\text{HNO}_3:\text{CIB}$ increases to 12:1 and 16:1 the amounts of DNCIB after 5 h are even greater and equal to 80.8 wt.% and 95.7 wt.%, respectively. However, after 10 h the amount of DNCIB is decreased as the catalyst presumably undergoes slow deactivation.

The influence of catalyst amount on nitration yield with substrate molar ratio $\text{HNO}_3:\text{CIB} = 12:1$ was further examined. The greater amount of catalyst with retaining the reactor geometry causes contact time between substrate and catalyst to be extended. The longer contact time results in increase in amount of DNCIB from 80.8 wt.% to 85 wt.% after first 5 h. After 10 h of the process CIB conversion to DNCIB increases to 94.5 wt.%. This indicates that greater amount of catalyst provides greater amount of acid active centers which enables to obtain higher reaction yield. The research showed that examined catalyst may be used in the DNCIB synthesis in continuous nitration process. In the reaction with 10 g of the catalyst and twelve-fold excess of nitric acid carried out for 10 h the summary yield to DNCIB is as high as 90 wt.%.

Table 5Chlorobenzene nitration in continuous process with various substrate molar ratios $\text{HNO}_3:\text{CIB}$ (5 g of catalyst, 80°C).

Substrate molar ratio $\text{HNO}_3:\text{CIB}$	Time (h)	Product composition (wt.%)		CIB Conversion (wt.%)
		MNCIB	DNCIB	
10:1	5	72.1	27.9	100
	10	33.3	66.4	100
12:1	5	19.2	80.8	100
	10	41.6	58.2	100
12:1, 10 g	5	15.0	85.0	100
	10	5.0	94.5	100
16:1	5	4.3	95.7	100
	10	13.1	86.8	100

4. Conclusions

A novel catalyst system – $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ – was examined in toluene and chlorobenzene nitration in continuous process. The catalytic system possesses very active surface Brönsted acid centers that enable effective nitration of toluene to DNT in one-stage process (96 wt.% of DNT in the product) and in mild conditions i.e. at room temperature and only with ten-fold excess of nitric acid. On the other hand, in chlorobenzene nitration greater amounts of nitric acid and higher temperature are required, however, only twelve-fold excess of nitric acid is needed to obtain as high yield to DNCIB as 95 wt.%.

To summarize, $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ catalyst has been shown to be very effective in toluene and chlorobenzene nitration that can be carried out in mild conditions in the more eco-friendly way. The greatest advantage is undoubtedly the organic solvent and sulfuric acid elimination from the process. All these qualities can make nitration reaction more ecological and cheaper process.

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