



## Dinitrotoluene Synthesis Using Solid State Catalysts – $\text{MoO}_3/\text{SiO}_2$ and $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$

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**Abstract:** Dinitrotoluene (DNT) has a lot of applications. It is mainly used in the production of polyurethane forms. Other uses include the explosives industry. It is converted to trinitrotoluene (TNT), or used as an additive in propellants.

The main aim of these researches was to obtain DNT in one stage process with solid acid catalyst and nitric acid. The solid catalysts were composed of transition metal oxide ( $\text{MoO}_3$ ) and silica gel. One of them was modified by phosphoric acid ( $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ ). The addition of phosphoric acid to these catalysts enhances catalytic properties and gives new structures on the surface – mixture of  $\text{MoO}_3$  and 12-molybdophosphoric acid. The activity of two catalysts in toluene nitration was compared.

Higher yields of DNT were obtained in shorter time and with lower excess of  $\text{HNO}_3$  using modified catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  than using catalyst  $\text{MoO}_3/\text{SiO}_2$ . The very high yield of DNT (85%) was obtained in the reaction with only tenfold excess of nitric acid with 10 g of  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ . The way of regeneration of the catalyst system  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  was found and time of storing was examined.

**Keywords:** toluene nitration, dinitrotoluene, solid catalyst, heteropolyacid

### Introduction

Nitration of toluene is very important process in the chemical industry. Dinitrotoluene (DNT) is very important product of nitration. DNT has big application as the substrate in manufacture of toluene diisocyanate (TDI). TDI is produced in large scale, because it is used in production of polyurethanes, these plastics are produced in large scale in the world. DNT is also used as additives in gun powder, propellants and explosive mixtures.

DNT is obtained by toluene nitration with a mixture of concentrated nitric and sulphuric acids [1]. Sulphuric acid is quite good catalyst of nitration because it improves the yield of nitration more than twice. Moreover, sulphuric acid aids the ionization of  $\text{HNO}_3$  to the nitronium ion (nitrating agent), and binds the water formed in the reaction. However, there is a need for burdensome ecologically utilization of the spent nitration acids (a mixture of sulphuric and nitric acid). There is also a need for the recycling of sulphuric acid. Purification and recycling introduce a lot of pollution and extra costs. The mixture is not enough effective to provide two nitro groups into aromatic compounds in one-stage and in mild conditions, therefore DNT is obtained in two-stage process.

New ecologic and economic trends suggest searching for novel catalyst systems. The catalyst should be selective, efficient and allow providing two nitro groups to aromatic ring in one step [2].

The objects of scientific studies are solid acid catalysts. Solid acid has on its surface some strong acidic centres capable of generating a nitronium ion. There are a lot of advantages of these catalysts: ease separation of product and catalyst separation from reaction medium, possibility of regeneration, high activity and selectivity, small quantities of hazardous waste. It was shown that the solid acids are effective catalyst in nitration [3-7].

The interest of these studies are the catalysts that are composed of transition metal oxide ( $\text{MoO}_3$ ) and silica gel [8, 9]. The best properties and the highest activity in toluene nitration exhibits catalyst system 15%  $\text{MoO}_3/\text{SiO}_2$  [8]. In literature, it was found that it was possible to improve acid properties of catalysts by using phosphoric acid. From that reason the catalyst system 15%  $\text{MoO}_3/\text{SiO}_2$  modified by  $\text{H}_3\text{PO}_4$  was examined. The purpose of the modification was to obtain the catalytic system that allows decreasing the excess of nitric acid in toluene nitration to DNT.

In this work the comparison of these two catalysts ( $\text{MoO}_3/\text{SiO}_2$  and  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ ) in toluene nitration to DNT is made.

## Materials and Methods

### General

Materials: toluene (pure), fuming nitric acid (pure), silica gel ( $\text{SiO}_2$ ), ammonium molybdate tetrahydrate [ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ] (pure), ethylene dichloride (pure), phosphoric acid (85%, pure), magnesium sulfate anhydrous (pure), sodium hydrogen carbonate (pure). All materials were taken from POCH Gliwice, Poland (except for  $\text{SiO}_2$  purchased from Małtwy, Poland).

Analysis of the reaction products was made using gas chromatography with a Perkin-Elmer Auto System XL and a PE-5 column.

Raman spectra were recorded on Nicolet Almega Dispersive Raman Spectrometer.

### **Catalyst MoO<sub>3</sub>/SiO<sub>2</sub> preparation [9]**

1.83 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O is dissolved in 15 mL 3% H<sub>2</sub>O<sub>2</sub> at room temperature. The solution thus prepared is applied to 8.5 g SiO<sub>2</sub> and dried at 110 °C for 24 h in a dryer; it is calcined at 300 °C for 18 h to obtain MoO<sub>3</sub> deposited on the carrier surface.

### **Catalyst H<sub>3</sub>PO<sub>4</sub>/MoO<sub>3</sub>/SiO<sub>2</sub> preparation**

An amount of ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) was dissolved in 3% H<sub>2</sub>O<sub>2</sub> at room temperature. Appropriate amount of the salt was taken to obtain 15% of MoO<sub>3</sub> of the mass of the catalyst. The solution thus prepared was applied to SiO<sub>2</sub> (grains 0.6-1mm) and dried in a drying oven at 110 °C till the mass stabilized. Next, the calcination was conducted at 300 °C in an air stream for 18 h to obtain oxide (MoO<sub>3</sub>) on the support surface. Solution of phosphoric acid (1 mole of acid on 12 mole of MoO<sub>3</sub>) was applied by wet impregnation to catalyst made in the first step. Re-calcinations were conducted in the same conditions and time.

### **Nitration process**

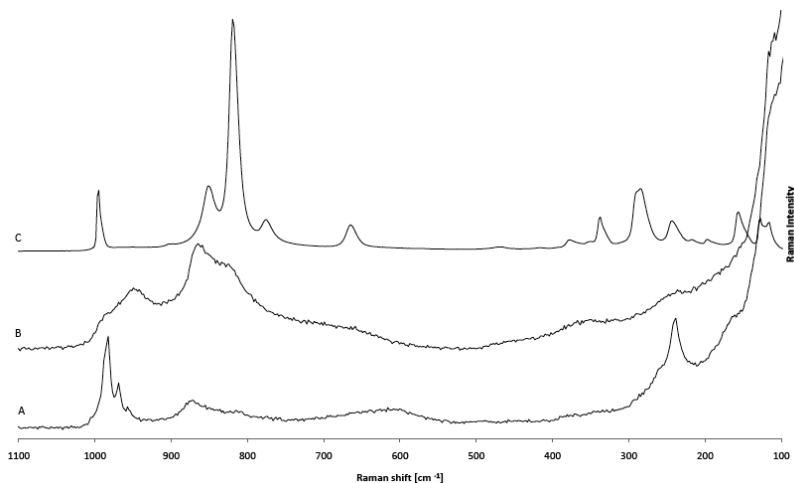
Into a three-necked flask equipped with a magnetic stirrer, a reflux condenser and a dropping funnel; catalyst (5 or 10 g), solvent (ethylene dichloride, 10 mL) and fuming HNO<sub>3</sub> were introduced. Toluene and solvent (12 mL) were placed in the dropping funnel. Upon drop wise addition of the funnel contents (for ca. 10 min) the reaction was continued to proceed at set temperature for set time. On completion of the reaction the catalyst was filtered and washed off with little solvent. The filtrate was shaken with aqueous sodium hydrogen carbonate (NaHCO<sub>3</sub>), then with distilled water, and finally dried over magnesium sulfate anhydrous (MgSO<sub>4</sub>).

## **Results and Discussion**

### **Description of catalyst systems - MoO<sub>3</sub>/SiO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>/MoO<sub>3</sub>/SiO<sub>2</sub>**

In the work two catalysts were used: the catalyst (MoO<sub>3</sub>/SiO<sub>2</sub>) and the catalyst modified by phosphoric acid (H<sub>3</sub>PO<sub>4</sub>/MoO<sub>3</sub>/SiO<sub>2</sub>). Structures on the modified catalyst surfaces were determined by the Raman spectroscopic analysis (Figure 1).

The catalyst  $\text{MoO}_3/\text{SiO}_2$  is obtained by calcinations of ammonium molybdate. Decomposition of molybdate occurs during calcinations. Precise description of catalyst system  $\text{MoO}_3/\text{SiO}_2$  is given in [8].



**Figure 1.** Raman spectra of the molybdenum compounds on the surface of catalyst system  $\text{H}_3\text{PO}_4/\text{oO}_3/\text{SiO}_2$ .

The modification of catalyst  $\text{MoO}_3/\text{SiO}_2$  by phosphoric acid allows obtaining various molybdenum compounds on the surface: molybdenum oxide ( $\text{MoO}_3$ ), polymolybdates and 12-molybdophosphoric acid (HPM). The catalyst does not have homogeneous layer on the surface. The spectra show sample of the same catalyst, but the spectra were taken from three different places on surface. The bands on the first spectra (Figure 1A) corresponds to HPM. The bands: 987, 970, 866, 600, 240  $\text{cm}^{-1}$  indicate Keggin structure of HPM, what is in accordance with literature [10]. The second spectrum (Figure 1B) indicates polymolybdates: 950, 870-820, 650, 350, and 236  $\text{cm}^{-1}$  [11]. Furthermore, on the surface is present molybdenum oxide (Figure 1C) in two crystal structures  $\alpha\text{-MoO}_3$  (994, 820, 670  $\text{cm}^{-1}$ ) and  $\beta\text{-MoO}_3$  (848, 773  $\text{cm}^{-1}$ ) [12, 13]. It is very probable that on the surface are present polyphosphates which have been formed due to excess of phosphoric acid [14]. The bands on the spectra from polyphosphates are not visible because they probably overlap with bands from polymolybdates. In summary, on the surface there is heterogeneous layer which consists of  $\text{MoO}_3$ , domains of HPM and monolayer of polymolybdates and polyphosphates. The catalyst system in this form was used in toluene nitration.

**Influence of substrate ratio  $\text{HNO}_3$ :toluene on the yield of DNT in toluene nitration with catalysts:  $\text{MoO}_3$  [8, 9] and  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$** 

The influence of nitric acid excess on the yield of DNT in toluene nitration with  $\text{MoO}_3/\text{SiO}_2$  and  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  is described. The results of the reactions are shown in Table 1.

The yield of nitration is almost the same in all reactions listed in Table 1. Higher yields of DNT were obtained in shorter time and with lower excess of  $\text{HNO}_3$  with modified catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  than with catalyst  $\text{MoO}_3/\text{SiO}_2$  at similar conditions. Modification of the catalyst  $\text{MoO}_3/\text{SiO}_2$  by phosphoric acid improves the catalyst effectivity. 22.7 wt.% of DNT in the products of the reaction was obtained in the nitration with substrates ratio only 1.5:1  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  catalyst.

Moreover, in the reaction with threefold excess of nitric acid 43.7 wt.% of DNT was obtained, whereas in the reaction with  $\text{MoO}_3/\text{SiO}_2$  in the same conditions only 14.4 wt.% of DNT was obtained.

85 wt.% of DNT was obtained in the reaction with tenfold excess of nitric acid(V) with  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  after 2.5 h. Similar amount of DNT was obtained with eightfold excess of  $\text{HNO}_3$  with catalyst  $\text{MoO}_3/\text{SiO}_2$ , but the reaction lasted 24 h.

The catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  changed the selectivity of the toluene nitration. The isomer 2,4-DNT was obtained in larger amounts (2,4-DNT/2,6-DNT ratio is almost two times higher than it was in nitration with  $\text{MoO}_3/\text{SiO}_2$ ).

Toluene nitration to DNT occurs only in the presence of nitronium cation ( $\text{NO}_2^+$ ). Therefore it is recommended to use large excess of nitric acid. Nitronium agent ( $\text{NO}_2^+$ ) is generated from fuming nitric acid in the autoprotection reaction. Moreover, the catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  is strong Brønsted acid (the proton catalyst effect), which allows to obtain high concentrations of nitronium ion in short time. In nitration with using nitric acid and  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  there are two positive effects which facilitate the  $\text{NO}_2^+$  obtaining. The concentration of nitronium ion is relatively high which makes the nitration more efficient.

**Influence of amount of the catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  on the yield of DNT in toluene nitration**

In the study on influence of the amount of the catalyst -  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  - on toluene nitration yield, the reactions with 10 and 5 g of the catalyst were examined. The reactions were carried on with two various excess of nitric acid (tenfold and sixteen-fold excess). The study results are listed in Table 2.

It can be seen that the conversion of toluene is almost 100 wt.%. The amount of DNT is increasing with the amount of the catalyst. It can be seen that

**Table 1.** The influence of molar substrate ratio  $\text{HNO}_3$ :toluene on the yield of DNT (Conditions: 10 g of catalyst, 2.5 h, room temperature). MNT – mononitrotoluenes, NT – nitrotoluene, ratio p/o – ratio p-NT/o-NT

Catalyst	Mole ratio $\text{HNO}_3$ -toluene	Yield [%]	Yield of MNT [%]	Composition of MNT			Ratio p/o	Yield of DNT [%]	Composition of DNT			Ratio 2,4-/2,6-
				o-NT	m-NT	p-NT			2,4-DNT	2,6-DNT	3,4-DNT	
$\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$	1.5:1	95.8	77.3	44.6	2.2	41.1	1.2	22.7	86.3	1.7	-	6.3
	3:1	94.4	56.3	40.3	2.3	32.3	1.4	43.7	84.4	15.6	-	5.4
	6:1	95.7	28.1	26.7	2.8	71.2	2.7	71.9	82.9	16.8	0.4	4.9
	10:1	99.9	15	25.3	15.3	59.3	2.3	85	84.2	11.6	4.0	7.2
	16:1	99.9	0.8	54.1	0.4	45.5	0.84	99.2	83.3	15.3	1.4	5.5
$\text{MoO}_3/\text{SiO}_2$	1.5:1	100	100	55	-	45	1.0	-	-	-	-	-
	3:1	100	85.6	46.6	2.1	51.3	1.1	14.4	77.1	22.9	-	3.4
	8:1 (24h)	100	12.5	11.8	10.9	77.3	0.2	87.5	70.7	29.3	-	2.4
	16:1	100	0.1	50.0	-	50.0	1.0	99.9	78.6	21.4	-	3.7

**Table 2.** The influence of amount of the catalyst -  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  on the yield of DNT in the reaction with two various excess of nitric acid (Conditions: room temperature, 2.5 h). MNT – mononitrotoluenes, NT – nitrotoluene, ratio p/o – ratio p-NT/o-NT, ratio 2,4-/2,6- – ratio 2,4-DNT/2,6-DNT

Mole ratio $\text{HNO}_3$ :toluene	Amount of catalyst [g]	Yield [%]	Yield of MNT [%]	Composition of MNT			Ratio p/o	Yield of DNT [%]	Composition of DNT			Ratio 2,4-/2,6-
				o-NT	m-NT	p-NT			2,4-DNT	2,6-DNT	3,4-DNT	
10:1	5	99.9	69.6	32	30.4	32.8	1.0	30.4	81.9	10.5	7.6	7.8
	10	99.9	15	3.8	85	8.9	2.3	85	84.2	11.6	4.0	7.2
16:1	5	100	11.8	0.04	trace	99.9	999	88.2	81.9	18	0.1	4.6
	10	100	0.8	54.1	0.4	45.5	0.84	99.2	83.3	15.3	1.4	5.5

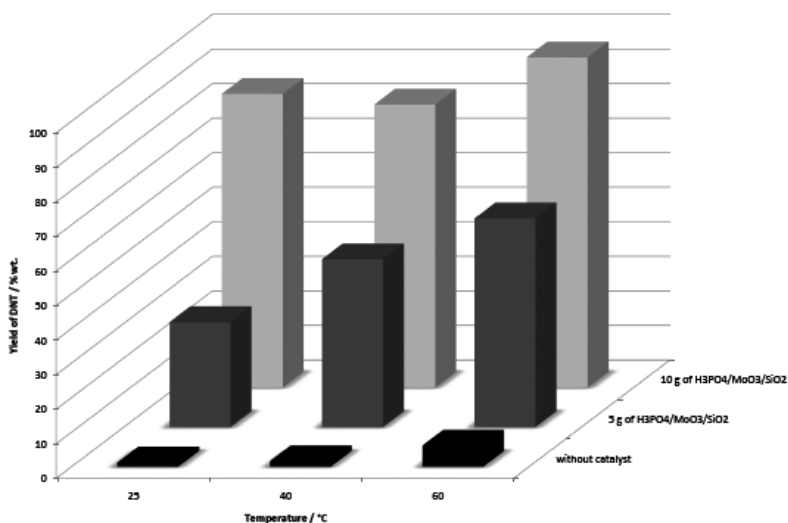
in reaction with 16-fold excess of nitric acid and 5 g of catalyst the obtained amount of DNT is similar to the amount of DNT obtained in the reaction with 10-fold excess of  $\text{HNO}_3$  and 10 g of catalyst.

The reduction of the amount of the catalyst decreases the yield of DNT. However, it should be emphasized that in the reaction with only 5 g of  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  the obtained yields of DNT were relatively high, 30.4 wt.% of DNT, at 25 °C for 2.5 h reaction.

In the reaction with 10 g of  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  and tenfold excess of  $\text{HNO}_3$  the obtained yields of DNT was satisfactory. Further studies on DNT synthesis were carried on with tenfold excess of nitric acid at higher temperatures.

### Influence of temperature on the yield of DNT in toluene nitration with $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$

The influence of reaction temperature was examined for tenfold excess of nitric acid and various amounts of catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  (without catalyst, 5 and 10 g). The yield of DNT is presented in Figure 2.



**Figure 2.** The influence of amount of the catalyst -  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  and temperature of reaction on the yield of DNT. (Conditions: 10:1 =  $\text{HNO}_3$ :toluene, 2.5 h).

The highest yield was obtained in the reaction with 10 g of the catalyst at 60 °C. 95.6 wt.% of DNT in 2.5 h reaction was achieved. The selectivity of the nitration was stable and 2,4/2,6 ratio was in the range of 6-8. The yields of DNT in the

nitration without catalyst, with using only nitric acid, were low even at 60 °C.

It was noticed that the influence of the amount of the catalyst was stronger than the temperature influence. The larger amount of the catalyst enables to decrease the temperature of the process. It is possible to obtain various composition of the product by the changing temperature or amount of the catalyst.

### Storing of catalyst $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$

The catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  was stored in a closed container for twelve days. The results of the reaction with 5g of the catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  and substrates ratio  $\text{HNO}_3$ :toluene 1.5:1 are presented in Table 3.

**Table 3.** The influence of storing on activity of catalyst system  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  (Conditions: (1.5:1 =  $\text{HNO}_3$ :toluene, room temperature, 2.5 h). MNT – mononitrotoluenes, NT – nitrotoluene, ratio p/o – ratio p-NT/o-NT

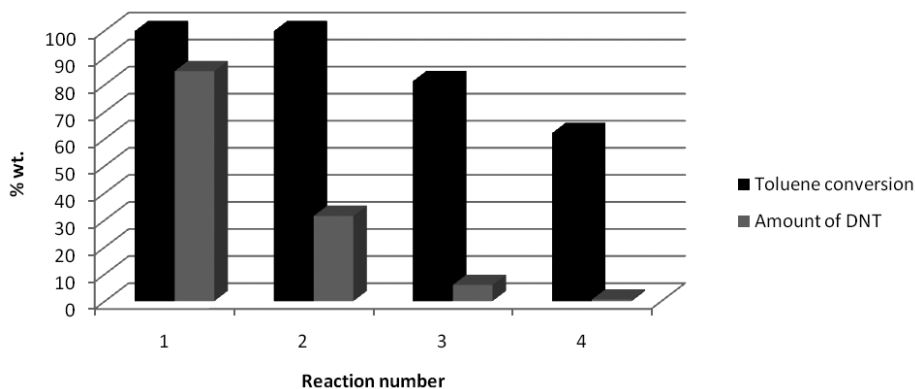
Days of storing	Yield, [%]	Yield of MNT, [%]	Composition of MNT			Ratio p/o	Yield of DNT, [%]
			o-NT	m-NT	p-NT		
0	99.6	97.2	45.8	1.5	52.6	1.15	2.8
1	99.6	95.7	45.4	1.6	53.0	1.17	4.3
5	99.9	97.5	46.0	1.5	52.4	1.14	2.5
12	97.6	94.3	45.4	1.6	53.0	1.17	5.7

The catalyst during storing in the closed container was not losing its characteristics. The yield and selectivity of reaction remains at similar level. The catalyst could be kept for two weeks without changing its quality.

### Reusing of the catalyst $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$

The same sample of the catalyst ( $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ ) was used in few reactions with substrates ratio ( $\text{HNO}_3$ :toluene) 10:1. It can be seen in Figure 3 that the yield of DNT was decreasing; therefore the activity of the catalyst system was decreasing.



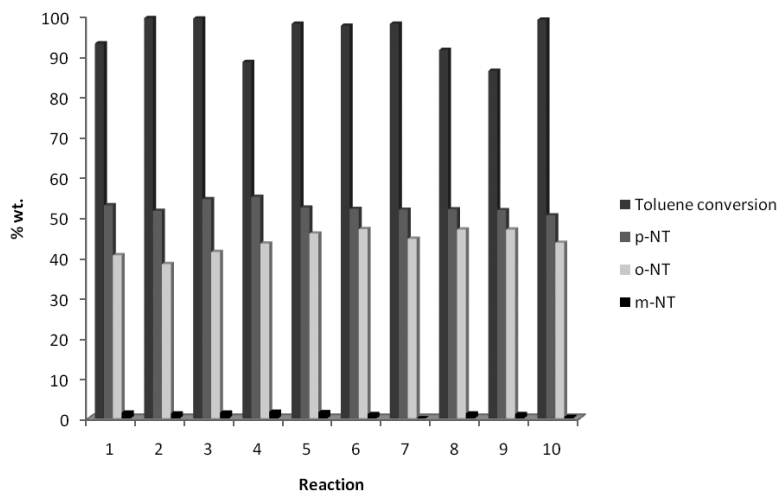


**Figure 3.** The yields of the toluene nitration in the subsequent reactions performed with the same catalyst.

The catalyst after each reaction was dried in the air. In the first two reactions the yield of the nitration maintained the same level. Only in the fourth reaction the yield was decreased to 60 wt.%. However, the amount of DNT was significantly decreasing. The catalyst crystals adsorb water (water from the air and obtained during the reaction) and this causes dilution of the nitric acid used in the next nitration. The dilution results in the decrease of the yield of the toluene nitration to DNT. From that reason it was necessary to find the method of the catalyst regeneration.

### Regeneration of the catalytic system $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$

The various methods of the regeneration of the catalyst system  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  were examined. The most efficient method was: washing off with solvent, drying in a drying oven at 110 °C, applying the solution of phosphoric acid (the same amount that was used in the first preparation), drying in a drying oven and heating at 300 °C for 1 h. The reactions with using 5 g of the catalyst and substrates ratio 1.5:1 were examined. The results of the toluene nitration with using regenerated catalyst are shown in Figure 4. It is shown that regeneration is possible and efficient. After 10 reactions the yield of toluene nitration was retained at the similar level.



**Figure 4.** Toluene conversion and composition of mononitrotoluenes in toluene nitration with regenerated catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  (Conditions: 1.5:1 =  $\text{HNO}_3$ :toluene, 2.5 h).

## Conclusions

This research work has shown that the catalyst  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  is efficient catalyst system in toluene nitration to DNT with using nitric acid in one-step process. The modified catalysts demonstrate better properties in toluene nitration than catalyst  $\text{MoO}_3/\text{SiO}_2$ . The yields of DNT are higher and obtained in shorter time for lower excess of nitric acid.

It is worth emphasizing that the selectivity of nitration is high and 2,4-DNT (more desirable isomer of DNT because of its using in manufacture of polyurethanes) was obtained in larger amount.

The better characteristics of  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$  in toluene nitration is caused by compounds and structures obtained on the surface. There are higher amount of polymolybdates. Moreover there are polyphosphates and domains of HPM.

The highest yield was obtained in conditions: 10 g of the catalyst –  $\text{H}_3\text{PO}_4/\text{MoO}_3/\text{SiO}_2$ , reaction time 2.5 h and temperature 60 °C. Furthermore, the method of regeneration was shown. These studies indicate the further way of using the solid catalyst modified by phosphoric acid in continuous process of toluene nitration. These research shows that it is possible to obtain DNT in simple and relatively more ecological way.

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