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# NITRATION OF AROMATIC COMPOUNDS ON SOLID CATALYSTS

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# NITRATION OF AROMATIC COMPOUNDS ON SOLID CATALYSTS

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## ABSTRACT

o-Xylene, phenol and toluene were nitrated with 100% nitric acid on $MoO_3/SiO_2$, $WO_3/SiO_2$, $TiO_2/SiO_2$, and $TiO_2–WO_3/SiO_2$ systems. Phenol and toluene were nitrated with yields higher than 90%, and the 10% and 15% $MoO_3/SiO_2$ catalysts were most active in the nitration of o-xylene. The most active catalysts exhibited the para-position selectivity of nitration.

## INTRODUCTION

The idea of the use of the "solid" nitric acid and a "solid" sulphuric acid in nitration reactions has its roots in the attempts to obtain systems in which separation of the product from the catalyst is easy so that the product is free of the catalyst. Moreover, in the case of substituted phenyl rings, the *para* substitution should be a preferred course of the nitration reaction in these systems. Examples of such

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systems are in particular 65% $HNO_3/SiO_2$ (1) and $H_2SO_4/SiO_2$ (2,3) systems. Here silica gel is a neutral ($pK_a = 7$) if we consider the acid/basic properties—it doesn't exhibit strong acidic or basic sites (4) and should not activate the acids deposited. It is of interest therefore to modify the solid support so as to make the acid centres formed capable of activating nitric acid, for example, just as it does the sulphuric acid in the nitrating mixture.

According to the literature data, such modifications that yield acid centres on the silica gel surface involve doping of silica with titanium, molybdenum, or tungsten ions (5–15). Such systems were obtained in our studies in the nitration of toluene, o-xylene, and phenol using 100% $HNO_3$ and 65% $HNO_3$. Results of the studies on these reactions are presented in this paper.

## EXPERIMENTAL

### Preparation of Catalysts

Preparation of Silica

The solid support for the catalyst studied is silica gel $SiO_2$ (supplied by Mątwy). Grain size range: 0.5–0.2 mm and 1.0–0.5 mm. Silica was purified by a repeated extraction by boiling in concentrated hydrochloric acid to remove trace metals, followed by repeated extraction with boiling water to a pH ~7. The silica thus prepared was dried for 24 h in an oven at 110°C.

Preparation of Catalysts (Examples)

**$HNO_3/SiO_2$ catalyst** was prepared thus (1):

60 g $SiO_2$ is mixed with 140 mL of 8M $HNO_3$ for 2 h at room temperature. On filtering it is dried in the open air. The $HNO_3$ content is determined by titration of the filtrate with an 0.1M NaOH. The amount of the nitric acid adsorbed on silica equals the difference between the amount of the acid used and that of the acid present in the filtrate.

**15% $TiO_2/SiO_2$**

19.9 mL 15% $TiCl_3$ solution in 10% HCl (Merck) is applied to 8.5 g $SiO_2$. It is then dried in a dryer at 110°C for 2 h, then calcined at 600°C in an air stream for 18 h to obtain $TiO_2$ on the surface of the carrier.

**15% $WO_3/SiO_2$**

6.23 g $(NH_4)_2$ $WO_4 * 8H_2O$ (pure-POCh Gliwice) is dissolved in 15 mL 3% $H_2O_2$ at room temperature. The solution thus prepared is applied to 8.5 g $SiO_2$ and dried at 110°C for 24 h in a dryer. It is then calcined at 600°C in a stream of air for 18 h to obtain $WO_3$ on the carrier surface.

**15% $V_2O_5/SiO_2$**

1.92 g $NH_4VO_3$ (pure-POCh Gliwice) is dissolved in 15 mL 3% $H_2O_2$ at room temperature. The resultant solution is applied to 8.5 g $SiO_2$ and, on drying at 110°C for 24 h in a dryer, it is calcined at 250°C for 18 h to obtain $V_2O_5$ deposited on the carrier surface.

**15% $MoO_3/SiO_2$**

1.83 g $(NH_4)_6Mo_7O_{24}*4H_2O$ (pure-POCh Gliwice) is dissolved in 15 mL 3% $H_2O_2$ at room temperature. The solution thus prepared is applied to 8.5 g $SiO_2$ and, on drying at 110°C for 24 h in a dryer, it is calcined at 550°C for 18 h to obtain $MoO_3$ deposited on the carrier surface.

**15% $TiO_2$–$WO_3/SiO_2$**

0.83 g $(NH_4)_2WO_4*8H_2O$ (pure-POCh Gliwice) is dissolved in 15 mL 3% $H_2O_2$ at room temperature. The solution thus prepared is applied to 9.8 g of the previously prepared catalyst 15% $TiO_2/SiO_2$ and dried at 110°C for 24 h in a dryer. It is then calcined at 600°C in a stream of air for 18 h to obtain $WO_3$ on the carrier surface.

## Physicochemical Studies of the Catalysts

### Determination of Acidity of the Catalysts Prepared

Hirschler indicators were used to determine the acidity of the catalysts prepared, which are employed to determine selectively the strength of the Brönsted type (proton) acid centres and are correlated with the acid strength corresponding to a given concentration of sulphuric acid. This allows us to assign an analogous nitrating strength to the system $H_2SO_4/HNO_3$ and solid acid/$HNO_3$, when both acids, the solid acid and the sulphuric acid of a given concentration, cause the color of an indicator to change.

The results obtained indicate that all the catalysts studied have Bröensted centres of an $H_R$ strength corresponding to a 50% $H_2SO_4$ concentration. Only the

*Table 1.* Properties of the Catalysts Used

| Hirschler Indicator* h | pKa | Corresponded $H_2SO_4$ Concentration | Color | |
|---|---|---|---|---|
| | | | Acid Form | Basic Form |
| Benzyl alcohol | −18.1 | 93 | yellow | colorless |
| Diphenylcarbinol | −13.3 | 77 | yellow | colorless |
| Triphenylcarbinol | −6.63 | 50 | yellow | colorless |

*The indicators used were in the form of 0.1% solutions in toluene (POCh Gliwice).

catalysts 10% and 15% $MoO_3/SiO_2$ have the centres of a higher acidity strength $H_R$ corresponding to an acidity strength of a 77% $H_2SO_4$.

### Determination of the $HNO_3$ Concentration in $CCl_4$ Solutions over the Catalysts Studied

The $HNO_3$ concentration in $CCl_4$ solutions over the catalysts examined were studied for the amounts of the solvent, catalyst, and the nitric acid used in the nitration study by adding the acid to the carbon tetrachloride over the catalyst. After 5 min the solvent was filtered off, which was then extracted with water (10 mL). The presence of acids in the extract was detected against phenolphthalein.

The study performed for all the catalysts prepared showed no acids present in the extract.

## Nitration Reaction

The nitration reactions were carried out on the basis of the literature data (16) initially under water-free conditions.

### o-Xylene and Toluene Nitration

Immediately before the reaction the catalyst was heated for 1.5 h in a stream of air at 250°C and subsequently cooled in dry argon.

Into a 100-mL three-neck flask equipped with a magnetic stirrer and a dropping funnel are introduced 10 mL of dry $CCl_4$, 10 g of the catalyst, and 0.43 g (6.8 mmol) of 100% $HNO_3$. In the dropping funnel o-xylene (0.42 g–4.0 mmol) or toluene (0.37 g–4.0 mmol) and $CCl_4$ (17 mL) are placed. On the dropwise addition of the funnel content (for ca. 10 min), the reaction is carried out at room temperature for 2.5 h. Then the catalyst is filtered off and washed with some $CCl_4$, which was added to the filtrate. The $CCl_4$ solution was washed with a few portions of aqueous $NaHCO_3$, then several times with water, dried with $MgSO_4$, and examined by GLC.

### Phenol Nitration

The catalyst is introduced into 8M $HNO_3$ at a weight ratio of 3:7 and stirred for 2 h at room temperature. On filtration the catalyst is dried in the air. The content of the nitric acid adsorbed on silica is determined by titration of the filtrate with an NaOH solution.

The acid used in the reaction is taken in a 110% excess of the theoretical amount needed.

The catalyst (1 g) with the adsorbed $HNO_3$ and $CH_2Cl_2$ (45 mL) were placed in the flask. Then 0.18 g (2.0 mmol) phenol was added. The reaction is allowed to proceed for 3 min at room temperature. On completion of the reaction the catalyst is filtered off and washed with a little $CH_2Cl_2$, which was added to the filtrate. The reaction products are analyzed by GLC.

Other reaction conditions are presented as a footnote of the tables.

## Analysis of the Reaction Products

For the determination of the conversion of substrates and composition of the nitration products, gas liquid partition chromatograph was used.

In the analysis of nitro-o-xylenes and nitrophenols, we used a CHROM-5 gas chromatograph (with a CI-100 computing integrator) and a chromatographic column 10% OV-101/chromosorb PAW DMCS.

In the analysis of mono- and dinitrotoluenes, we used a Perkin-Elmer Auto System XL instrument and a PE-5 chromatogrephic column.

## Results

### o-Xylene Nitration

The nitration of o-xylene using a 100% nitric acid was carried out with or without catalytic systems of a content of 5, 10, and 15% by wt. of individual metal oxides, i.e. $MoO_3$, $WO_3$, $TiO_2$, and $V_2O_5$ on silica. The $TiO_2/SiO_2$ system with its variety enriched with 2% by wt. of $WO_3$ was examined.

The nitration reaction occurring in the presence of $HNO_3$ alone affords the nitro-derivatives in an 80% yield. By isomers, the yield is slightly higher for 3-nitro-o-xylene (52%), whereas for 4-nitro-o-xylene, it is 48%.

The use of the $MoO_3/SiO_2$ catalyst increases the reaction yield, which increases with the molybdenum trioxide on silica (15% $MoO_3$–98% yield). The catalyst also affects the formation of the 4-nitro-o-xylene derivative in an overwhelming amount.

The $WO_3/SiO_2$ system acts more as an inhibitor in the o-xylene nitration reaction. As little as 5% of $WO_3$ reduces the nitration yield, compared with the non-catalyzed reaction, from 80% to 66%. More tungsten oxide on silica causes a further drop in reaction yield. Here, the 3-nitro-o-xylene is obtained in a higher yield.

Also, the $TiO_2/SiO_2$ catalyst makes the yield of the o-xylene nitration reaction drop in comparison with the yield of the reaction occurring without the catalyst. Here, however, a rise in the yield with the amount of the titanium dioxide supported on silica is observed for the nitroderivatives. At 15% of $TiO_2$, less 4-nitro-o-xylene isomer (41%) is found to form, whereas the 3-nitro-isomer was produced in greater quantity.

The enrichment of the $TiO_2/SiO_2$ system in $WO_3$ results, in that the reaction for 15% $TiO_2$–2% $WO_3/SiO_2$ proceeds analogously as the nitration by means of the nitric acid alone, both as concerns yield and composition of products. At a greater $TiO_2$ content, a drop in the reaction yield and the formation of equal amounts of both nitro-o-xylene isomers are observed.

***Table 2.*** Nitration of o-Xylene on Solid Catalysts

| % by wt. of Metal Oxide on $SiO_2$ | Yield [%] | 3-nitro-o-xylene [%] | 4-nitro-o-xylene [%] | Isomer 3- to Isomer 4-Ratio |
|---|---|---|---|---|
| no catalyst | 80 | 52 | 48 | 0.92 |
| 5% $MoO_3$ | 59 | 52 | 48 | 0.92 |
| 10% $MoO_3$ | 90 | 43 | 57 | 1.33 |
| 15% $MoO_3$ | 98 | 44 | 56 | 1.27 |
| 5% $WO_3$ | 66 | 49 | 51 | 1.04 |
| 10% $WO_3$ | 55 | 52 | 48 | 0.92 |
| 15% $WO_3$ | 21 | 53 | 47 | 0.89 |
| 5% $TiO_2$ | 21 | 52 | 48 | 0.92 |
| 10% $TiO_2$ | 36 | 52 | 48 | 0.92 |
| 15% $TiO_2$ | 39 | 59 | 41 | 0.96 |
| 5% $TiO_2$–2% $WO_3$ | 80 | 48 | 52 | 1.18 |
| 10% $TiO_2$–2% $WO_3$ | 78 | 50 | 50 | 1.00 |
| 15% $TiO_2$–2% $WO_3$ | 73 | 50 | 50 | 1.00 |
| 15% $V_2O_5$ | 16 | 56 | 44 | 0.79 |

The $V_2O_5/SiO_2$ system fails as an o-xylene nitration catalyst, as it reduces the reaction yield from 80% (no catalyst) to 16%. Here 3-nitro derivative forms in prevalence.

The nitration of o-xylene under these conditions afforded mononitroderivatives only. Activity of the catalytic systems (based on the nitration reaction yield) declines in the following order: $MoO_3 > 100\% \ HNO_3 > TiO_2–WO_3 > WO_3 > TiO_2 > V_2O_5$.

For the $MoO_3/SiO_2$ and $V_2O_5/SiO_2$ systems, the o-xylene nitration was carried out at elevated temperatures, 40°C and 60°C. The results obtained are shown in Table 3.

o-Xylene nitration using 100% nitric acid at temperatures 20° and 40°C essentially does not affect the o-xylene conversion, which is ca. 70%. At 60°C the conversion drops to 54%. Selectivity of the reaction to obtain 3- and 4-nitro-o-xylene is independent of the temperature. In the products invariably the 3-nitroisomer is in excess, although the para/ortho ratio increases from 0.92 at 20°C to 0.96 at 60°C. The raised temperature also affords o-nitrotoluene as a result of ypso-nitration (5).

The $V_2O_5/SiO_2$ system at 20°C affords a very low yield. Only if the temperature is raised to 40° and 60°C does the yield attain 50–60%. If the product obtained at 20°C contains 3-nitro-o-xylene in excess, at 40°C concentrations of both isomers are the same. Besides these derivatives, o-nitrotoluene is produced also in a ca. 1.5% amount.

The use of the $MoO_3/SiO_2$ catalyst containing 15% $MoO_3$ allows us to obtain as much as 99% yield in o-xylene nitration at 20°C, whereas raising temperatures to 40° and 60°C yields a complete conversion of the substrate, with a rising selectivity to 4-nitroisomer (para/ortho = 1.4 at 60°C) and to ypso nitration products, i.e. o-nitrotoluene.

Another variable of the o-xylene nitration reaction studied was the effect of the amount of the catalyst used.

If less than 7 g of the 15% $MoO_3/SiO_2$ catalyst is used, the reaction yield decreases significantly, although the reaction continues to proceed on the catalyst

***Table 3.*** o-Xylene Nitration on Solid Supported Catalysts at Various Temperatures

| Reaction | No Catalyst | | | 15% $V_2O_5/SiO_2$ | | | 15% $MoO_3/SiO_2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature | 20°C | 40°C | 60°C | 20°C | 40°C | 60°C | 20°C | 40°C | 60°C |
| Conversion [%] | 70 | 77 | 54 | 16.5 | 61.5 | 51.5 | 99 | 100 | 100 |
| o-NT [%] | – | 3.5 | 4.0 | – | 1.5 | 1.5 | 7.0 | 8.5 | 8.5 |
| 4-NOX [%] | 34 | 33 | 24.5 | 7.0 | 30.5 | 25.5 | 52 | 51.5 | 53.5 |
| 3-NOX [%] | 36 | 35 | 25.5 | 9.0 | 30.0 | 25.0 | 40.0 | 40.5 | 38.0 |
| 4/3-nitro | 0.92 | 0.94 | 0.96 | 0.77 | 1.02 | 1.02 | 1.30 | 1.28 | 1.40 |

***Table 4.*** o-Xylene Nitration Catalyzed with Variable Amounts of 15% $MoO_3/SiO_2$ Catalyst

| Catalyst [g] | 1 g | 3 g | 5 g | 7 g | 10 g |
|---|---|---|---|---|---|
| Conversion [%] | 71.5 | 71.5 | 71.5 | 92 | 99 |
| o-NT [%] | 2.0 | 2.0 | 2.0 | 3.0 | 7.0 |
| 4-NOX [%] | 37.5 | 39.5 | 41.5 | 50.0 | 52.0 |
| 3-NOX [%] | 32.0 | 30.0 | 28.0 | 39.0 | 40.0 |
| 4-nitro/3-nitro | 1.17 | 1.32 | 1.48 | 1.28 | 1.30 |

surface. Evidence of this may be the excess of the 4-nitro-o-xylene derivatives in the nitration products. A fall in the quantity of the side product, o-nitrotoluene, that forms there is also observed.

For the reaction conducted with 1 g of the 15% $MoO_3/SiO_2$ catalyst at 60°C, the reaction time was extended from 2.5 to 6 h. The nitration yield obtained was 78% (71.5% at 20°C). Longer reaction time does not significantly affect the yield or composition of the products; however, a rise in o-nitrotoluene formed was noted.

Attempts were made to utilize the same catalyst for o-xylene nitration. The catalyst used was 15% $MoO_3/SiO_2$. The yield slightly decreases following each successive reaction. The repeated use of the catalyst shifts selectivity of the nitration process; relatively more 3-nitroderivative is produced, yet the 4-nitro-o-xylene isomer still prevails in the products. Results of the experiments are shown in Table 5.

## Phenol Nitration

The same catalytic systems were used in the reaction of nitration of phenol with 65% nitric acid. A very high activity of all the catalysts used was noted to lead to a reaction yield of over 90%. For the $WO_3/SiO_2$ system, very high selectivity of the nitration reaction at para position was observed to obtain p-nitrophenol in a yield higher than 90% in the products. The use of the $TiO_2/SiO_2$ catalyst produces a mere ca. 49% of the isomer.

***Table 5.*** o-Xylene Nitration with the 15% $MoO_3/SiO_2$ Catalyst Used Repeatedly

| | Reaction I | Reaction II | Reaction III | Reaction IV |
|---|---|---|---|---|
| Conversion [%] | 99 | 88.5 | 79.5 | 74.0 |
| o-NT [%] | 8.5 | 4.0 | 1.0 | 1.0 |
| 4-NOX [%] | 51.0 | 48.0 | 41.0 | 38.0 |
| 3-NOX [%] | 39.0 | 36.0 | 37.0 | 35.0 |
| 4-nitro/3-nitro | 1.29 | 1.15 | 1.12 | 1.09 |

*Table 6.* Phenol Nitration on Supported Catalysts

| % by wt. Oxide on $SiO_2$ | Yield [%] | o-nitrophenol [%] | p-nitrophenol [%] | Para to Ortho Isomer Ratio |
|---|---|---|---|---|
| 5% $WO_3$ | 97 | 9 | 91 | 10.11 |
| 10% $WO_3$ | 92 | 10 | 90 | 9.00 |
| 15% $WO_3$ | 99 | 8 | 92 | 11.50 |
| 5% $MoO_3$ | 99 | 15 | 85 | 5.67 |
| 10% $MoO_3$ | 93 | 22 | 78 | 3.55 |
| 15% $MoO_3$ | 98 | 33 | 67 | 2.03 |
| 5% $TiO_2$ | 90 | 51 | 49 | 0.96 |
| 10% $TiO_2$ | 90 | 52 | 48 | 0.92 |
| 15% $TiO_2$ | 91 | 51 | 49 | 0.96 |
| 5% $TiO_2$–2% $WO_3$ | 93 | 23 | 77 | 3.35 |
| 10% $TiO_2$–2% $WO_3$ | 92 | 21 | 79 | 3.76 |
| 15% $TiO_2$–2% $WO_3$ | 95 | 49 | 51 | 1.04 |

The results achieved also show that the p-nitrophenol content in the nitration product decline with the rise in content of the individual metal oxides (i.e. $MoO_3/SiO_2$, $TiO_2/SiO_2$, $TiO_2$–$WO_3/SiO_2$), supported on silica. The reaction performed resulted merely in mononitro-derivatives of phenol.

The systems studied behaved very similarly concerning the yield of the nitro-derivative obtained. They differ merely in the selectivity of para-nitration.

The highest selectivity was found in the 5–15% $WO_3/SiO_2$ system yielding in the products over 90% of p-nitrophenol. A slightly lower selectivity is displayed by the molybdenum catalyst, from 85% to 67% of para-isomer and, in this case, a drop in selectivity is observed in favor of para-nitration, with the $MoO_3$ supported on silica. The $TiO_2$–$WO_3$ behaves analogously.

The $TiO_2/SiO_2$ catalyst shows the same selectivity for the ortho- and para-nitration, irrespective of the $TiO_2$ content on the silica support. The isomers are obtained in nearly the same yield.

The selectivity order can be arranged thus: $WO_3 > MoO_3 > TiO_2$–$WO_3 > TiO_2$.

## Toluene Nitration

Catalyst, 15% by wt. of $MoO_3$ supported on silica, was studied in the reaction of toluene nitration using 100% nitric acid.

Initially the effect of rising temperature of the reaction on the yield and selectivity of toluene nitration were investigated. At as low a temperature as 20°C, toluene becomes completely converted to afford respective nitro-derivatives

***Table 7.*** Toluene Nitration using a 15% by wt. $MoO_3$ Silica-supported Catalyst*

| | No Catalyst | | | 15% $MoO_3/SiO_2$ | | |
|---|---|---|---|---|---|---|
| Reaction Temperature | 20°C | 40°C | 60°C | 20°C | 40°C | 60°C |
| Conversion [%] | 83 | 87 | 83.5 | 100 | 100 | 100 |
| Nitrobenzene [%] | 0.27 | 1.54 | 1.96 | – | – | – |
| o-nitrotolune [%] | 49.6 | 53.2 | 48.7 | 55 | 51.2 | 50.15 |
| m-nitrotoluene [%] | 2.2 | – | – | – | – | – |
| p-nitrotoluene [%] | 31.1 | 32.3 | 32.9 | 45 | 48.8 | 49.85 |
| p/o ratio | 0.62 | 0.61 | 0.68 | 0.82 | 0.95 | 0.99 |

*Reaction conditions: $HNO_3$/toluene = 1.5:1, 10 g catalyst, 22 ml $CCl_4$, reaction time 2.5 h.

(Table 7), when, for reactions without catalyst, only about 80% conversion of toluene is observed. Increase of temperature increases the p/o ratio in both cases. This ratio is always higher for the catalyzed reactions. Any ypso-product was obtained when the catalyst was used.

In the nitration reactions performed merely mononitrotoluene derivatives were obtained. Subsequently, the effect of the catalyst on the formation of toluene nitro-derivatives containing more than one nitrogroup, was studied. A greater excess of nitric acid was used to achieve this goal. The results are compared in Tables 8–10.

An attempt to make dinitrotoluene in a 100% yield for a slight stoichiometric excess of $HNO_3$ at an $HNO_3$ to toluene mole ratio of 3:1 failed, both when the

***Table 8.*** Toluene Nitration with a 15% $MoO_3/SiO_2$ Catalyst for a $HNO_3$ to Toluene Mole Ratio of 3:1*

| | No Catalyst T = 20°C Time = 24 h | 15% $MoO_3/SiO_2$ T = 20°C Time = 2.5 h | 15% $MoO_3/SiO_2$ T = 20°C Time = 24 h | 15% $MoO_3/SiO_2$ T = 60°C Time = 6 h |
|---|---|---|---|---|
| Conversion [%] | 100 | 100 | 100 | 100 |
| Nitrobenzene [%] | – | – | 1.23 | 0.88 |
| o-nitrotoluene [%] | 33.36 | 39.95 | 26.38 | 39.04 |
| p-nitrotoluene [%] | 30.51 | 43.90 | 37.21 | 40.56 |
| p/o ratio | 0.91 | 1.10 | 1.41 | 1.03 |
| Dinitrotoluenes | 17.84 | 14.38 | 32.44 | 16.8 |
| 2,6-DNT [%] | 23.53 | 22.9 | 25.61 | 20.16 |
| 2,4-DNT [%] | 76.47 | 77.1 | 74.39 | 79.84 |

*Reaction conditions: Amount of the catalyst was 10 g, 22 ml $CCl_4$.

*Table 9.* Toluene Nitration with a 15% $MoO_3/SiO_2$ Catalyst for a $HNO_3$ to Toluene Mole Ratio of 8:1*

| | No Catalysts Time = 24 h | 15% $MoO_3/SiO_2$ Time = 24 h | 15% $MoO_3/SiO_2$ Time = 48 h | 15% $MoO_3/SiO_2$ Time = 72 h |
|---|---|---|---|---|
| Conversion [%] | 100 | 100 | 100 | 100 |
| o-nitrotoluene [%] | 26.87 | 1.48 | – | – |
| p-nitrotoluene [%] | 23.89 | 9.66 | 2.77 | 2.68 |
| p/o ratio | 0.88 | 6.54 | – | – |
| Dinitrotoluenes | 45.17 | 87.46 | 96.64 | 97.31 |
| 2,6-DNT [%] | 23.61 | 29.31 | 25.79 | 23.61 |
| 2,4-DNT [%] | 76.39 | 70.69 | 74.21 | 76.39 |
| 2,6/2,4 ratio | 0.31 | 0.41 | 0.34 | 0.39 |

*Reaction conditions: Amount of the catalyst was 10 g, 22 ml $CCl_4$, t = 20°C.

nitric acid was used alone, and in the present of the 15% $MoO_3/SiO_2$ catalyst. After 24 h of the reaction, dinitrotoluenes were obtained in a yield of only 27% when $HNO_3$ was used alone, and in 33% with a catalyst present in the reaction environment. Raised temperature failed to give any desirable results.

An increased $HNO_3$ excess in relation to toluene as 8:1 for the nitration with $HNO_3$ alone affords an increased yield of dinitroderivatives, the amount for the catalyzed system being twice the amount for the non-catalyzed reaction.

The nitration reaction with the catalyst present in the reacting system is rather slow and after at least 48 h toluene converted to its dinitroderivatives attains over 90%.

*Table 10.* Toluene Nitration with a 15% $MoO_3/SiO_2$ Catalyst for an $HNO_3$ to Toluene Mole Ratio of 16:1*

| | No Catalyst Time = 2 h | 15% $MoO_3/SiO_2$ Time = 0.5 h | 15% $MoO_3/SiO_2$ Time = 1 h | 15% $MoO_3/SiO_2$ Time = 2 h |
|---|---|---|---|---|
| Conversion [%] | 100 | 100 | 100 | 100 |
| o-nitrotoluene [%] | 18.98 | 0.56 | 0.40 | 0.12 |
| p-nitrotoluene [%] | 14.50 | 0.56 | 0.40 | 0.12 |
| p/o ratio | 0.71 | – | – | – |
| Dinitrotoluenes | 61.24 | 99.44 | 99.60 | 99.88 |
| 2,6-DNT [%] | 23.39 | 22.86 | 20.91 | 21.43 |
| 2,4-DNT [%] | 76.61 | 77.14 | 79.09 | 78.57 |
| 2,6/2,4 ratio | 0.30 | 0.29 | 0.26 | 0.27 |

*Reaction conditions: Amount of the catalyst was 10 g, 22 ml $CCl_4$, t = 20°C.

In increased mole ratio to 16:1 leads to an abrupt rise in the nitration reaction, affording nearly 100% conversion of toluene to its dinitroderivatives in as short a time as 0.5h. Under these conditions, the uncatalyzed reaction affords dinitrotoluene in a yield of 61.24% after 2 h.

The results obtained indicate that both an increased $HNO_3$/toluene mole ratio and the presence of $MoO_3/SiO_2$ catalyst have a favorable effect on the toluene dinitration. A major component of the products obtained is 2,4-dinitrotoluene. As a component of the reaction mixture with other dinitrotoluenes, it is formed invariably in a constant yield independent of the $HNO_3$/toluene mole ratio. About threefold more of the 2,4-dinitrotoluene is formed, compared with the 2,6- dinitroderivative.

## Discussion

If the nitration of o-xylene with 100% $HNO_3$ for a $HNO_3$/o-xylene ratio equalling 1.5:1 is assumed as reference for the same process by carried out in the presence of catalytic systems studied, the catalysts may be divided into three groups:

1. 10% and 15% $MoO_3/SiO_2$ catalysts, in the presence of which the nitration process proceeds in the respective yields of 90% and 98%, which is higher than when nitrating with neat 100% $HNO_3$ and with a higher selectivity towards nitration at position 4-, determined as a ratio of the amount of isomers 4- to that of isomer 3- of mononitro-o-xylene, the value of which is above 1.2;
2. 5% $MoO_3/SiO_2$, 5–15% $TiO_2$–2% $WO_3/SiO_2$ catalysts, in the presence of which the nitration proceeds with yields above 65%, which is less than for the nitration with 100% $HNO_3$ only, yet with the selectivities towards nitration at position 4- than for the acid used alone;
3. 10–15% $WO_3/SiO_2$, 5–15% $TiO_2/SiO_2$ and 15% $V_2O_5/SiO_2$, in the presence of which the nitration with 100% $HNO_3$ proceeds with yields below 55% and the selectivities towards nitration at position 4- that are the same or even lower than for the nitration with 100% $HNO_3$ only.

The catalysts of the first group mentioned are the only ones that have on their surface the proton acidity centres of a strength corresponding to the concentration of the hydrogen cations in $H_2SO_4$ of at least 77%, and it is those that are most likely responsible for the generation of the $NO_2^+$ cations from the activated nitric acid adsorbed on the surface of those catalysts. This effect is stronger here than in the case of the neat 100% $HNO_3$. The nitronium cations here are adsorbed on the catalyst surface and it is where the nitration reaction proceeds in the first place, just as for the reactions of nitration in the presence of solid acids (the para effect) and $H_3PO_4/P_2O_5$ system described in the literature (5).

On the surface of the second group catalysts, there occur only the proton acidity centres corresponding to the proton cation concentration in a 50% $H_2SO_4$, which, just as in the 50% $H_2SO_4/HNO_3$ system, are not capable of producing the nitrating agents of an efficiency observed for 100% $HNO_3$. A higher selectivity towards nitration at position 4- indicates that the nitration reaction in the presence of those catalysts proceeds to a perceptible degree, on the catalyst surface.

The catalysts of the third group, which significantly impair yield of the nitration with 100% $HNO_3$, also possess the proton centres of a strength corresponding to that of the hydrogen cations in 50% $H_2SO_4$. Here, however, the selectivity towards the nitration at position 4- is the same as, or even lower than, for the nitration with 100% $HNO_3$ only. This suggests that the nitration reaction proceeds in the presence of these catalysts in a solvent, of which the $HNO_3$, originally adsorbed on the surface, desorbs. The reaction in a solvent occurs at a much slower rate than it does on the catalyst surface.

Despite the fact that in a solvent decanted from above the grains of the catalysts studied, no perceptible amounts of nitric acid could be detected, it is quite likely that it is desorbed in particular in the presence of the substrates and reacts with them immediately. The process should occur with a relatively higher intensity for the third group of the catalysts studied.

When the o-xylene nitration reaction temperature is raised from 20° to 60°C, the reaction yield decreases when conducted with 100% $HNO_3$. Selectivity of the nitration at position 4-, on the other hand, increases and the products of ypso-nitration of o-toluene are observed to form.

If the nitration process is conducted in the presence of a 15% $MoO_3/SiO_2$, the temperature rise causes the reaction yield to increase to 100%, the selectivity towards the nitration at position 4-, but also causes an increase in ypso-nitration affording 8.5% o-nitrotoluene in the reaction products, that is twice as much as previously. This indicates that raising the nitration temperature, as well as the presence of the molybdenum catalyst, favors the formation of xylene cation radicals to a greater degree at the expense of the Wieland complexes (5), the nitration of which proceeds at positions with an increased unpaired electron density (5), in the case of o-xylene in the position 4-, twice bigger than in the position 3-. It also increases the nitration at position 4- additionally to the effect of the catalyst surface.

A relatively high ratio of the 4- to 3- isomers obtained from nitroxylenes demonstrates that the nitration reaction in these systems proceeds primarily on the catalyst surface regardless of its amount. The nitration reaction conducted against 1 g of the catalyst at 60°C where higher yields were observed to 78%, and a higher selectivity towards ypso-nitration with no change in selectivity towards the 3- and 4- isomers, as compared to the reaction run at 20°C, suggest that the differences in yields for the systems with 1–10 g of the catalyst during the nitration at 20°C are due to thermal effects. For the catalyst amounts of 10 and 7 g, local overheating in the catalyst bulk are likely to occur, resulting in a higher catalyst activity and its ypso-nitration selectivity. For the systems with a decreased catalyst amount, the catalyst concentration in the suspension is lower, which results in a better heat exchange that prevents overheating. This results in a reduced nitration rate, decreased ypso-nitration selectivity, and even an observed rise in para-nitration selectivity. Already for the catalyst amount of 1 g a relatively greater effect than on the supported catalyst is observed in the nitration reaction, which manifests itself in a respectively lower value of the isomer 4- to isomer 3- ratio.

A subsequent use of the same catalyst, on its washing with carbon tetrachloride after each reaction, leads to its gradual deactivation. This effect results in a reduced amount of the products whose formation is ascribed to the reaction occurring on the catalyst surface, notably a decrease in the isomer 4- content and in the ypso-nitration products, at nearly unaltered content of isomer 3- in the products. This suggests that the deactivated catalyst does not adsorb or activate nitric acid, causing the nitration process to occur in the solvent.

Toluene nitration using 100% $HNO_3$ in the presence of 15% $MoO_3/SiO_2$ catalyst over a temperature range of 20°–60°C proceeds with a 100% conversion, which is ca. 20% higher than in the nitration without the catalyst. A rise in the reaction temperature in either case results in an increased amount of the isomer 4- formed in the products, the effect being relatively more pronounced for the catalysed reaction. Nearly 1.5 times greater amount of this isomer for the catalyzed reaction is evidence that the reaction here goes primarily on the catalyst surface.

Attempts made to obtain dinitrotoluenes were successful when the $HNO_3$/toluene ratio was 16:1. Their yield of 99.44% was obtained just after 0.5 h of the reaction course for the catalyzed reaction. For the uncatalyzed reaction, a yield of 61.24% of these products is attained after 2 h of the reaction course. A further extension of the reaction in the presence of a catalyst up to 2 h affords a relatively greater amount of 2,4-dinitrotoluene. This suggests that here occurs the reaction of isomerization of the nitro group from the kinetically favored ortho-position to the thermodynamically more stable para-position.

The results demonstrate that the catalyst used in any of the cases studied generates more nitrating agents than are produced in the neat 100% $HNO_3$. This is favored by increasing the $HNO_3$/toluene ratio.

A 100% yield in the nitration of phenol using 65% $HNO_3$ in the presence of the catalysts that contain oxides of molybdenum, tungsten, and titanium supported on silica gel in analogous conditions as described in the literature (3) for the 65%$HNO_3/SiO_2$, for which the yield was 90%, showed that each of the catalysts studied generates and activates the nitrating agents in a more effective way than does nitric acid on silica alone. This is accountable by a higher acidity of these catalysts, due to the presence of the oxide modifiers used. The modifiers in the case of molybdenum oxide, and even more for tungsten oxide, yielded an exceedingly high selectivity of p-nitrophenol, which was above 90%. This is probably due to the superficial structures of these oxides that make up entities of a "tower-like" structure (17) with the proton centres at their base. It is likely that it is where the nitrating agents are generated and only the para-position of phenol can access them.

The nitrating agents in the systems studied should be the nitronium cations for the systems where the nitric acid of a suitable concentration is used and the nitrosyl cations for the systems with dilute acids. In either case the presence of the proton centres should favor their formation.

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