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**Mechanochemical Synthesis**

# Effect of process parameters on mechanochemical nitration of toluene

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## ABSTRACT

Aromatic compounds such as toluene are commercially nitrated using a combination of nitric acid with other strong acids. The process generates waste, which is difficult to handle and dispose of. A solventless process for mechanochemically nitrating toluene has been proposed recently, producing mononitrotoluene (MNT) with sodium nitrate as a source of nitrogen and molybdenum oxide as a catalyst. Here, this mechanochemical method of nitrating toluene is explored further to establish the effect of process parameters on the product yield. MNT yields exceeding 60% were achieved in different tests. A parametric study addressed the effects of milling time, temperature, milling media, and catalyst additives on the MNT yield and on formation of various by-products. Recovered amounts of MNT showed a maximum with milling time, which occurred earlier for smaller milling balls. However, the yield was reduced and reaction was slowed down when steel balls were replaced with finer glass beads. Overall recovery rate, including all by-products and unreacted toluene decreased after the maximum MNT yield, was observed. Milling temperature had only a weak effect on MNT formation but affected the formation of other aromatic by-products. Replacing various fractions of $MoO_3$ with fumed silica led to an increased yield of MNT for up to 30% of silica. The yield dropped when higher percentages of $MoO_3$ were replaced. The degree of refinement of $MoO_3$ by milling was quantified by measuring the surface area of the inorganic fraction of the milled material. The surface measurements were correlated with the product yield.

## Introduction

Nitration of organic compounds is necessary for a wide variety of applications. For example, most energetic materials are organic compounds with the nitro group as the oxidizer [1]. Nitrated aromatics are also widely used as solvents, dyes [2], pharmaceuticals [3], and perfumes [4]. For energetic materials, nitrotoluene is of particular interest because it is the first precursor in the synthesis of trinitrotoluene or TNT, a common explosive [5]. In addition, nitrotoluene is used in synthesis of toluidine,

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nitrobenzaldehyde, and chloronitrotoluenes, which are the intermediates for the production of dyes, resin modifiers, optical brighteners, and suntan lotions [6]. The nitrating agent for these reactions has traditionally been fuming nitric acid combined with another strong acid, e.g., sulfuric acid, perchloric acid, selenic acid, hydrofluoric acid, boron triflouride, or an ion-exchange resin containing sulfonic acid groups. These strong acids are catalysts that result in the formation of the nitronium ion, $NO_2^+$. Sulfuric acid is most common in industrial nitration because it is both effective and relatively inexpensive.

The common nitration methods have a number of disadvantages. Perhaps, most significant is the production of large quantities of spent acid which must be regenerated because its neutralization and disposal on a large scale are environmentally and economically unsound [7]. Another issue is the generation of considerable amounts of environmentally harmful waste during the purification of products [8]. Additional disadvantages include the hazards associated with handling the nitrating agents, as well as over nitration [9]. The reactions involving strong acids are not selective and yield a mixture of isomers, some of which are less desirable than others. For example, toluene nitration produces a mixture of mononitrotoluene (MNT) isomers with 55–60% of ortho- or o-MNT, 35–40% of para- or p-MNT, and 3–4% of meta-, or m-MNT [6]. This leads to large quantities of unwanted product because the demand for p-MNT is greater than for the other isomers [6, 10]. To increase the ratio of p- to o-isomers, nitration is commonly done in the presence of phosphoric acid or aromatic sulfonic acids. While the p/o ratio increases from 0.6 to 1.1–1.5 [6], additional environmentally harmful reactants are used. Another challenge associated with this reaction is the formation of oxidized by-products. The addition of a nitro group to the aromatic ring of toluene strongly activates its methyl group making it susceptible to oxidation. The oxidation is minimized in industrial toluene nitration by carrying it out at low temperatures [6]. In a batch process, for example, the acids are added at 25 °C and the reaction is carried out at 35–40 °C [6]. The total MNT yield in this reaction is 96% for a batch process, but most patents for continuous processes report yields of up to 50% [6].

Our previous study [11] established the feasibility of mechanochemical nitration of toluene using sodium nitrate as a source of nitronium ions and molybdenum oxide as an environmentally benign catalyst. It was observed that the MNT production was strongly affected by the relative ratios of the starting components, including $C_7H_8$, $NaNO_3$, and $MoO_3$. While MNT was formed, the yield was relatively low and substantial amounts of undesired by-products formed as well. The reaction mechanism had not been clarified. The objectives of the current work are therefore to improve the accuracy of product analysis, to identify experimentally the process parameters affecting yield and selectivity of MNT formation, and finally, to interpret the experimental parametric study of MNT production to elucidate the processes and reactions leading to the mechanochemical nitration of toluene.

## Experimental

Following our previous work [11], toluene was nitrated by mechanical milling with sodium nitrate and molybdenum oxide. The bulk reaction is shown in Eq. 1.

$$C_7H_8 + NaNO_3 \xrightarrow{MoO_3} C_7H_7NO_2 + NaOH \qquad (1)$$

Materials used in the experiments were toluene (Startex, solvent grade), molybdenum oxide $MoO_3$ (Alfa Aesar, 99.95%), and sodium nitrate (Alfa Aesar, 99%). Several milling runs were carried out with a fraction of $MoO_3$ substituted with silica. Two types of silica were used: fumed silica (Alfa Aesar, 99.8%) and quartz glass obtained by crushing quartz glass cylinders with a hammer and pre-milling it in a shaker mill for 5 min. The reactants were milled in a Retsch PM 400MA planetary mill using hardened steel vials and hardened steel balls or glass beads as milling media. The sizes of milling media varied as listed in Table 1.

**Table 1** Milling media

| Media | Diameter |
|---|---|
| Hardened steel balls | 1/2″ = 12.7 mm |
| | 3/8″ = 9.525 mm |
| | 1/4″ = 6.35 mm |
| | 1/8″ = 3.175 mm |
| Glass beads | 0.4–0.6 mm (average 0.5 mm) |
| | 0.088–0.149 mm (average 0.125 mm) |

## Milling details

The total mass of the solids in each vial was kept constant at 43.3 g; it included 1.67 g of sodium nitrate and molybdenum oxide with or without added silica. The volume of toluene was 0.5 ml for most runs, although several samples were prepared with 2 ml toluene. The mass of the milling media was 130 g for all runs, thus the ball to powder mass ratio (BPR) stayed constant at 3. Milling times varied from 0.5 to 4 h. All samples were milled at 400 RPM.

In all experiments, the vials were cooled using an air conditioner unit built in the planetary mill and set at 15.6 °C (60 F). The milling temperature was adjusted further by using custom-made cooling fins (see [12] for details) added to the vials and employing an intermittent milling protocol. The surface temperatures of the milling vial lids were measured during several runs using previously calibrated thermistors attached to the lids. The readings were taken at half-hour intervals throughout the runs. Details of the three used temperature control regimes and respective temperatures are listed in Table 2. The differences in the vial temperature caused by different milling protocols are around 20–25 °C. It is apparent that the milling media had no effect on the vial temperature except for the case of milling with 1/2″ steel balls. In the latter case, the temperature was reduced noticeably compared to all other milling media. Additional measurements (omitted from Table 2 for brevity) showed that replacing a fraction of $MoO_3$ with silica had no effect on the vial temperature for any of the temperature control regimes.

Based on the literature reports of aromatic nitration with fuming nitric acid where $MoO_3$ on silica support was used as catalyst [13], we investigated the possibility of toluene nitration by substituting part of the $MoO_3$ catalyst with silica. Several 2-h milling runs were carried out in the planetary mill with varying fractions of $MoO_3$ replaced with silica. 1/4″ hardened steel balls were used as milling media in all of these runs. All three temperature control regimes listed in Table 2 were used with fumed silica; only the intermediate protocol was used with quartz glass.

## Sample recovery

Reaction products were extracted with ethyl acetate (Alfa Aesar, 99.5%). Before extraction, the milling vials were allowed to cool for 20 min by being left in the mill with the air conditioner running. Each milling vial was then opened, and 150 ml of ethyl acetate was added to the vial. The vial was closed and placed back in the mill, where it was spun at 300 RPM for 5 min, with the balls remaining in the vial, in order to agitate the suspension. This suspension was stored for further analysis. In two experiments, samples were extracted using a water-cooled 500 ml Soxhlet extractor. The solvent was added into the milling vial and agitated at 300 RPM for 1 min. The resulting suspension was removed and added into the thimble of the extractor until it was filled. The thimble was placed in a beaker and kept there until the liquid fraction collected in the beaker. The procedure was repeated until the entire sample was filtered. Then, the thimble was placed into the extractor and the solution recovered from the beaker was placed into the extractor flask and boiled for 24 h with the aid of boiling stones.

## Sample analysis

Each suspension sample was stirred, and the solid fraction was separated by centrifuging for 5 min in a LW Scientific Ultra-8F centrifuge. The liquid fraction was analyzed in an HP 6890 gas chromatograph (GC,

**Table 2** Temperature control regimes of planetary mill experiments

| Milling balls (media) | | Temperature, °C for different milling protocols | | |
|---|---|---|---|---|
| Material | Diameter, inch (mm) | Intermittent milling, fins "Low" | Continuous milling, fins "Intermediate" | Continuous milling, no fins "High" |
| Glass | 0.125 mm | | 47.3 ± 3.3 | |
| Glass | 0.50 mm | | 44.8 ± 0.2 | 63.5 ± 3.2 |
| Hardened steel | 1/8 (3.175) | 19.0 ± 1.0 | 47.8 ± 2.9 | 68.2 ± 5.7 |
| Hardened steel | 1/4 (6.35) | 22.3 ± 5.5 | 47.0 ± 4.4 | 69.6 ± 2.7 |
| Hardened steel | 3/8 (9.525) | | 47.3 ± 3.7 | |
| Hardened steel | 1/2 (12.7) | | 34.2 ± 0.3 | 42.5 ± 11.7 |

heating profile: 40–250 °C at 5 K/min; split ratio: 10) coupled with HP G2350A mass spectrometer (MS). Product species were identified using the NIST Mass Spectral Library (NIST 08). Different data processing methods were used to evaluate concentrations of the products using the GC–MS output. In preliminary experiments, as in Ref. [11], the relative yield of MNT, $Y_{\mathrm{MNT,rel}}$, was estimated as

$$Y_{\mathrm{MNT,rel}} = \frac{\sum P_{\mathrm{MNT}}}{P_{\mathrm{Tol}} + \sum P_{\mathrm{products}}} \tag{2}$$

where $P$ indicates the integrated GC peaks, and the subscripts MNT, Tol, and products refer to MNT, toluene, and all identifiable products, respectively. Similar to Eq. 2, the relative yield of any species can be estimated for all products using their respective peak areas in the numerator. Using Eq. (2) to calculate the product yield introduces several potential errors. In addition to measurement uncertainties, any inaccuracy in the determination of the amounts of toluene and reaction products, whether due to losses or due to the presence of products that cannot be detected by GC–MS, lead to systematic overestimation of the MNT yield. In order to mitigate some of these uncertainties, the yield was determined relative to the amount of toluene introduced at the beginning of milling. This required calibration of the GC–MS measurements. A known amount of xylene (Sunnyside, solvent grade) was added to the ethyl acetate solution to serve as an internal standard for each subsequent measurement. Figure 1 shows a sample GC–MS plot featuring xylene and MNT peaks.

In addition to MNT peaks, benzaldehyde (labeled in Fig. 1) as well as two dimers: 2-methylphenyl-phenylmethanone and 4-methylphenyl-phenylmethanone (occurring at longer times than included in Fig. 1) were consistently observed as formed by-products. These species were accounted for when assessing the total recovery of the products of mechanochemical reaction from the milling vials, as discussed below.

The GC peak areas for MNT and toluene were calibrated using reference solutions of toluene, p-MNT (Sigma-Aldrich, 99%), and xylene in ethyl acetate. Actual concentrations could then be determined from the recorded calibration curves and peak ratios of MNT and toluene to xylene.

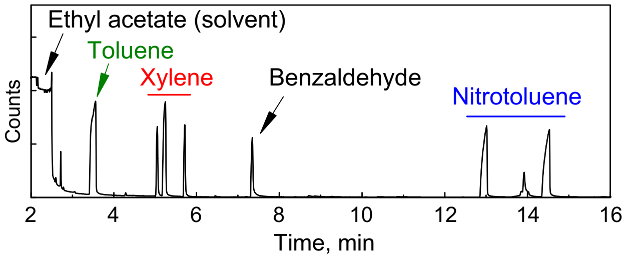

**Figure 1** Sample GC–MS trace of a processed sample with xylene added as an internal standard.

The absolute yield of MNT, $Y_{\mathrm{MNT}}$, was calculated as follows:

$$Y_{\mathrm{MNT}} = \frac{f_{\mathrm{MNT}}\left(\sum P_{\mathrm{MNT}} / \sum P_{\mathrm{xyl}}\right) \cdot C_{\mathrm{xyl}}}{C_{\mathrm{tol},0}} \tag{3}$$

where $f_{\mathrm{MNT}}$ indicates the calibration curve discussed above, $P_{\mathrm{xyl}}$ and $C_{\mathrm{xyl}}$ are the peak areas and the introduced concentration of xylene, respectively, and $C_{\mathrm{tol},0}$ is the initial toluene concentration at the beginning of milling.

The yield determined from Eq. (3) maybe lower than the true yield, because of incomplete recovery of products. Product recovery, $R$, was assessed as follows:

$$R = \frac{\sum_{\mathrm{products}} C_i}{C_{\mathrm{tol},0}} \tag{4}$$

where the sum in the numerator contains all toluene-derived species determined by GC–MS, including toluene itself. In this estimate, product species concentrations that were not explicitly calibrated were estimated by setting their respective calibration function, $f_i\left(\sum P_i / \sum P_{xyl}\right) = 1$. This leads to unspecified systematic errors, which can only be corrected if a specific calibration is performed for each species formed. However, the purpose of this analysis is the relative comparison between different runs; therefore, a repeatable systematic error was acceptable.

## Surface area

Surface area of the solid fraction of several samples was determined using Brunauer–Emmett–Teller (BET) nitrogen adsorption method. After extracting the organic phase, the solid (inorganic phase) was dried and degassed at 350 °C for 4.5 h. After degassing, the surface area of the samples was measured using nitrogen adsorption BET (Quantochrome Instruments Autosorb IQ ASIQM000000-6, 11 point adsorption measurement).

## Results

In preliminary experiments, milling times varied from 1 to 4 h, different milling media were used, and the relative MNT yield was obtained from Eq. (2). Significant relative yields of MNT varied in the range of 10–90% were observed for all milling conditions, including the experiments with glass beads as the milling media. Results with different milling media showed the lowest yields when 12-mm steel balls were used. The yields were also relatively low for glass beads. The highest yields were obtained for the milling times of 1–2 h when 3–10-mm diameter hardened steel balls served as the milling media. It was also observed that the recovery of the product using Soxhlet extractor was not more effective than using the solution agitated in the mill, respectively, and the latter approach was employed in all experiments discussed below.

All systematic experiments are summarized in Table 3. The highest observed mononitrotoluene yield exceeded 65%, and the ratio of para- to ortho-isomers was consistently above 1.

Observed trends are discussed in detail below.

### Effect of milling time and media

Absolute MNT yield calculated using Eq. (3) is shown in Fig. 2 for a set of experiments with varied milling times and milling media. The milling protocol employing continuous milling with cooling fins (leading to intermediate vial temperatures, see Table 2) was used in all experiments shown. No silica was used. It is observed that the highest MNT yields occur close to 1 h for runs using 1/4″ steel balls as the milling media. Results shown in Fig. 2 also suggest that the peak yield may occur at shorter times for 1/8″ steel balls, and possibly at longer times for larger steel balls, although additional measurements would be needed to confirm this. For any of the glass beads used, the yield is substantially lower than for any runs using steel balls for the set of measurements shown in Fig. 2.

To understand the reasons for the reduction in the MNT yield at longer milling times, clearly observed for the cases of 1/8″ and 1/4″ steel balls, consider data presented in Fig. 3. Results for 1/4″ steel balls, for which the highest MNT yield was observed, are examined closer. The recovery and MNT yield for that case are compared to the fraction of toluene left in the vial and the fractions of the consistently observed by-products. All concentrations were determined comparing the measured GC–MS peak areas of respective species to that of xylene, while accounting for the actual xylene concentration; then the fraction of each compound was assessed based on the starting amount of toluene, similar to Eq. (3). As noted earlier, because no xylene-based calibration was made for the by-products, the concentrations may include a systematic error. However, the main purpose of introducing such concentrations here is to observe their relative changes as a function of a process parameter, i.e., the milling time in Fig. 3. Therefore, a systematic error is acceptable, while all the data are processed consistently. Results in Fig. 3 show that most of toluene was consumed by the end of 1-h milling, when the highest MNT yield was observed. The highest MNT yield occurs at the same time when concentrations of all tracked by-products peak as well. At longer milling times, MNT concentration and the by-product concentrations decrease, while the toluene concentration remains negligible. The reduced recovery at longer milling times could represent either additional reactions in the milling vial with products that are not detectable by GC–MS, or physical losses during milling or the extraction procedure.

### Effect of temperature

Figure 4 shows the MNT yield after 2 h of milling as a function of effective milling temperature for 1/4″ steel balls. The error bars show standard deviations from repeat experiments. The overall yield is effectively constant with temperature. The toluene consumption is inversely proportional to the milling temperature, although most of toluene was consumed at all temperatures, consistent with the trends seen in Fig. 3. However, increased losses at higher temperatures cannot be ruled out. On the other hand, the formation of different by-products follows different trends. Benzaldehyde is more abundant at low temperatures, while its yield at the higher temperature is reduced. Conversely, the yield of both dimers consistently increases with temperature; a trend opposite to that observed for the total product recovery. Inspecting data in Table 3 show that the p/o ratio for the MNT isomers varies in the range of ca. 1.25–1.35 with a slightly greater p/o ratio at lower milling temperatures.

**Table 3** Summary of all systematic experiments

| Milling media sizes (steel balls) | Silica fraction (%) | Initial volume of toluene (mL) | Milling time (h) | Temp. regime (low, intermediate, high) | Est. temp. (°C) | Surface area ($m^2$/g) | MNT yield (%) | MNT p/o ratio |
|---|---|---|---|---|---|---|---|---|
| 1/2″ | | 0.5 | 0.5 | I | 31.6 | | 11.0 | 1.02 |
| 1/2″ | | 0.5 | 1 | I | 31.6 | | 21.1 | 1.07 |
| 1/2″ | | 0.5 | 2 | H | 50.6 | 10.8 | 23.3 | 0.64 |
| 3/8″ | | 0.5 | 0.5 | I | 47.3 | | 32.2 | 1.16 |
| 3/8″ | | 0.5 | 1 | I | 47.3 | | 54.8 | 1.15 |
| 1/4″ | | 0.5 | 0.5 | I | 49.8 | | 45.5 | 1.21 |
| 1/4″ | | 0.5 | 1 | I | 49.8 | | 67.3 | 1.25 |
| 1/4″ | 10 | 0.5 | 2 | L | 33.4 | | 33.4 | 1.36 |
| 1/4″ | 10 | 0.5 | 2 | I | 49.8 | | 31.8 | 1.40 |
| 1/4″ | 10** | 0.5 | 2 | I | 49.8 | | 23.0 | 1.41 |
| 1/4″ | 10 | 0.5 | 2 | H | 68.8 | | 44.4 ± 0 | 1.13 ± 0.12 |
| 1/4″ | 20 | 2 | 2 | I | 49.8 | | 9.7 | 1.14 |
| 1/4″ | 20 | 0.5 | 2 | H | 68.8 | | 44.2 | 1.12 |
| 1/4″ | 30 | 0.5 | 2 | L | 33.4 | 35.8 | 49.6 ± 7.2 | 1.34 ± 0.06 |
| 1/4″ | 30** | 0.5 | 2 | I | 49.8 | | 40.3 | 1.30 |
| 1/4″ | 30 | 0.5 | 2 | I | 49.8 | 45.8 | 55.4 ± 7.8 | 1.26 ± 0.01 |
| 1/4″ | 30 | 0.5 | 2 | H | 68.8 | | 61.7 | 1.37 |
| 1/4″ | 40 | 0.5 | 2 | H | 68.8 | | 55.4 | 1.13 |
| 1/4″ | 50 | 0.5 | 2 | L | 33.4 | | 36.4 | 1.25 |
| 1/4″ | 50 | 0.5 | 2 | I | 49.8 | | 42.9 ± 17.4 | 1.39 ± 0.02 |
| 1/4″ | 50** | 0.5 | 2 | I | 49.8 | | 12.1 | 1.00 |
| 1/4″ | 50 | 2 | 2 | I | 49.8 | | 10.6 | 1.14 |
| 1/4″ | 50** | 2 | 2 | I | 49.8 | | 7.5 | 1.13 |
| 1/4″ | 50 | 0.5 | 2 | H | 68.8 | | 26.7 ± 1.6 | 1.19 ± 0.13 |
| 1/4″ | 70 | 0.5 | 2 | I | 49.8 | | 4.5 | 1.47 |
| 1/4″ | 70** | 0.5 | 2 | I | 49.8 | | 8.3 | 1.01 |
| 1/4″ | 90 | 0.5 | 2 | I | 49.8 | | 0.3 | |
| 1/4″ | | 0.5 | 2 | L | 33.4 | 14.5 | 33.6 ± 11.6 | 1.34 ± 0.01 |
| 1/4″ | | 0.5 | 2 | I | 49.8 | 18.5 | 32.5 ± 7.6 | 1.36 ± 0.08 |
| 1/4″ | | 0.5 | 2 | H | 68.8 | 15.3 | 32.3 ± 1.4 | 1.25 ± 0.01 |
| 3/16″ | | 0.5 | 0.5 | I | 48.5 | | 42.0 | 1.19 |
| 3/16″ | | 0.5 | 1 | I | 48.5 | | 41.3 | 1.28 |
| 3/16″ | 30 | 0.5 | 2 | I | 48.5 | 44.8 | 48.5 | 1.26 |
| 3/16″ | 30 | 0.5 | 2 | L | 32.1 | 43.3 | 36.7 | 1.20 |
| 3/16″ | | 0.5 | 2 | L | 32.1 | 11.5 | 12.3 | 1.41 |
| 3/16″ | | 0.5 | 2 | I | 48.5 | 13.1 | 19.2 | 1.43 |
| 0.5* | | 0.5 | 0.5 | I | 44.6 | | 1.4 | 1.24 |
| 0.5* | | 0.5 | 1 | I | 44.6 | | 3.0 | 1.23 |
| 0.5* | | 0.5 | 2 | H | 63.6 | 15.4 | 20.6 | 1.17 |
| 0.125* | | 0.5 | 0.5 | I | 47.3 | | 2.5 | 1.11 |
| 0.125* | | 0.5 | 1 | I | 47.3 | | 3.5 | 1.30 |

*Glass beads, mm units

**Quartz glass instead of fumed silica

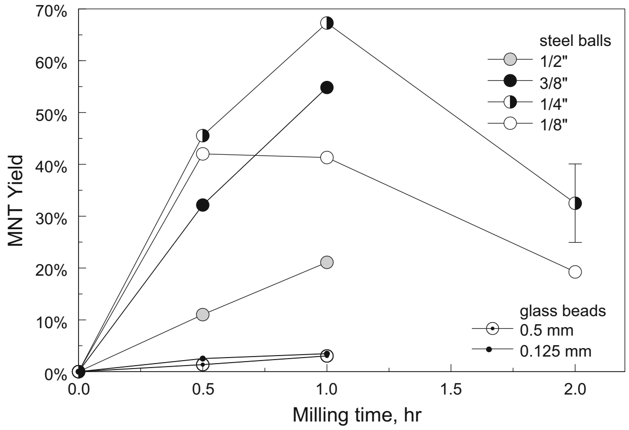

**Figure 2** Absolute MNT yield for different milling times and milling media. The intermediate temperature regime was used.

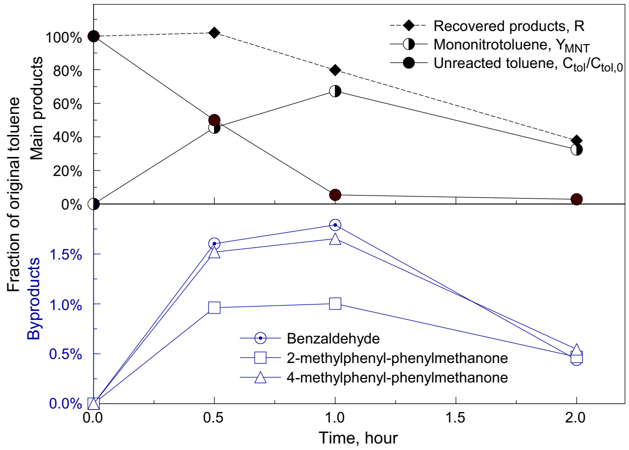

**Figure 3** Comparison of the total product recovery, absolute MNT yield, and depletion of toluene as a function of milling time with yield of significant by-products. 1/4″ steel milling balls are used with the intermediate temperature regime.

## Milling with $MoO_3$ and silica

The absolute MNT yield calculated using Eq. (3) is shown for multiple experiments performed at a fixed milling time of 2 h, in which a fraction of $MoO_3$ was replaced with silica. Different milling protocols were used resulting in different temperatures; both fumed silica and quartz glass were used in different runs. The results show clearly that the MNT yield is highest when about 30 wt% of $MoO_3$ is replaced with silica. This effect is the same for both fumed silica and quartz glass, although quartz glass gives systematically lower yields than fumed silica. Respectively, the experiments with quartz glass were performed using only one milling protocol. At different temperatures, the maximum yield is observed at about the same fraction of $MoO_3$ replaced with fumed silica. The lack of a pronounced effect of milling temperature on yield, observed in Fig. 4, is generally consistent with the results shown in Fig. 5. For both fumed silica and quartz glass, an increase in the silica content well above 30% causes a substantial reduction in the yield. Data in Table 3 show no correlation between p/o ratio of the produced MNT isomers and fraction of $SiO_2$ substituting $MoO_3$.

In Fig. 6, the MNT yield is plotted along with the recovery, yields of by-products, and amount of toluene left for different fractions of silica replacing $MoO_3$ for the set of experiments with 1/4″ steel balls. Initially, both MNT yield and recovery rate increase with greater amounts of silica used. Above about 30% silica, a clear trend of increased toluene concentration (along with the reduced MNT yield) is observed, indicative of an overall lower reaction rate caused by

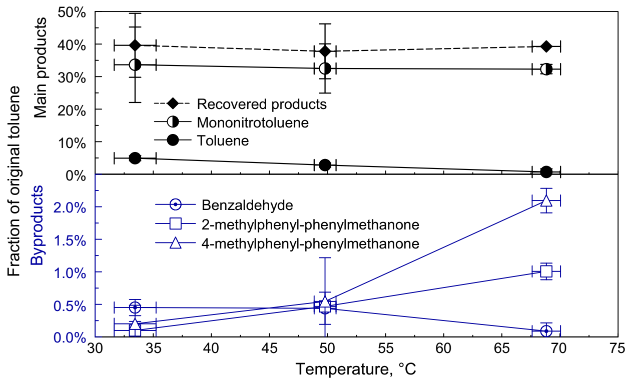

**Figure 4** Comparison of the total product recovery, absolute MNT yield, and depletion of toluene as a function of milling temperature with yield of significant by-products. 1/4″ steel balls are used with a milling time of 2 h.

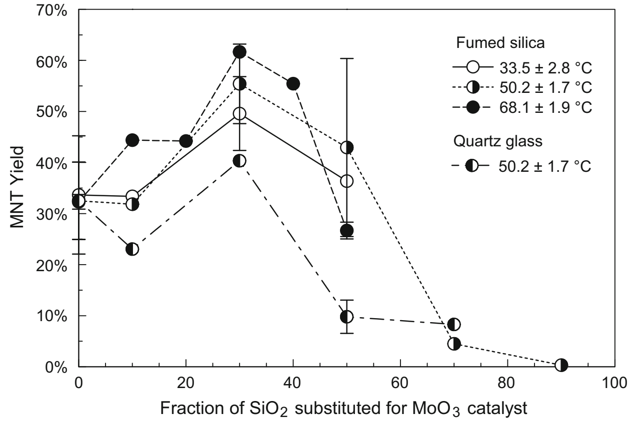

**Figure 5** Absolute MNT yield versus fraction of silica replacing $MoO_3$ for 2-h runs using 1/4″ steel balls as milling media.

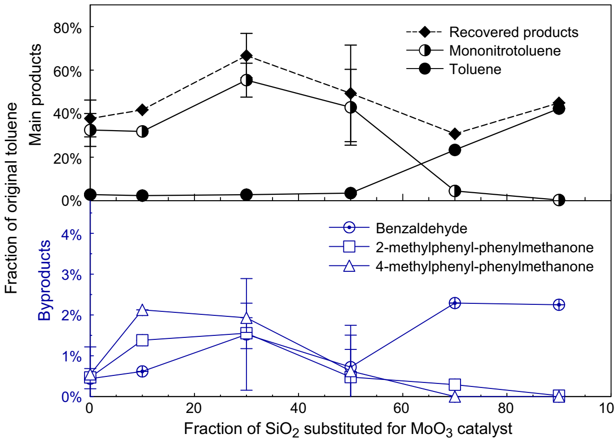

**Figure 6** Comparison of the total product recovery, absolute MNT yield, and depletion of toluene as a function of the added silica with yield of significant by-products. 1/4″ steel milling balls are used with the milling protocol leading to the intermediate temperature. Milling time is 2 h.

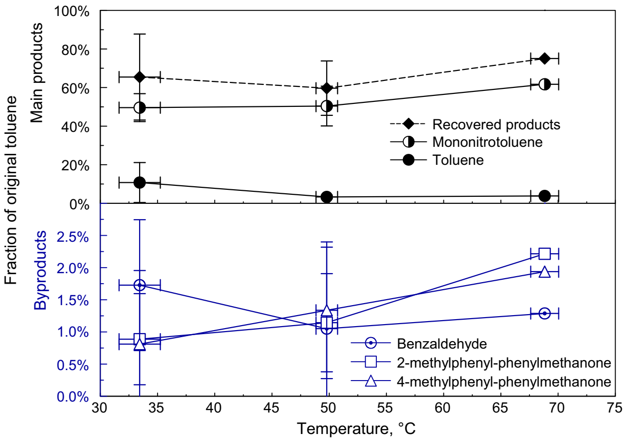

**Figure 7** Product recovery, absolute MNT yield, and toluene consumption as a function of milling temperature with yield of significant by-products when 30% of the $MoO_3$ catalyst is replaced with fumed silica. 1/4″ steel balls are used with the milling time of 2 h.

the dilution of $MoO_3$ catalyst. The trends observed for by-products are somewhat different: benzaldehyde forms preferentially at greater silica amounts. Both dimers form with a pattern closely following the formation of MNT. It is interesting that despite greater concentrations of unreacted toluene at high silica amounts, the recovery is relatively low.

Figure 7 shows product yields and recovery rates versus temperature for the experiments with 30% of the $MoO_3$ catalyst replaced by fumed silica. A weak positive trend in the MNT yield is observed. The dimeric by-products also increase with increasing temperature, similarly to the results in Fig. 4 when no silica was added. From Table 3, it can be noted that the p/o ratio increases slightly at reduced milling temperatures, consistent with the observation for experiments performed at different temperatures but without silica.

## Surface area measurements

Surface areas of the inorganic fraction of the milled samples were measured for several 2-h planetary mill runs with varying milling media, with and without silica. For the samples without silica, specific surface areas ranged from 10.4 to 18.5 $m^2/g$, whereas for the samples milled with 30% silica specific surface areas ranged from 35 to 45 $m^2/g$. The surface area of unmilled fumed silica was determined to be 484 $m^2/g$; thus, the surface area of the milled samples was significantly smaller than the sum of the surface areas of separate sample components. This indicates that silica was incorporated with the molybdenum oxide to form composite catalyst particles.

Figure 8 shows the MNT yields determined for a set of 2-h experiments with corresponding surface area measurements. This plot combines results obtained with different milling media, including samples prepared with and without 30% $SiO_2$ substituted for the $MoO_3$ catalyst. In addition, effective milling temperatures are indicated at each data point. There appears to be an overall positive correlation between specific surface area and MNT yield. As shown in Figs. 4 and 5, MNT yield may also be positively correlated with the milling temperature, although the effect is weak. No correlation between specific surface area and p/o ratio of the produced MNT isomers is detected from data in Table 3.

## Discussion

In previous experiments, primarily using a shaker mill [11], it was observed that the reaction yield increased substantially with an increase in solid (catalyst)-to-liquid (toluene) ratio. The present results, using a planetary mill enabled us to increase considerably the solid-to-liquid ratio and to achieve, respectively, higher yields.

Variations in the yield of MNT as a function of different process parameters observed in this study suggest that the mechanochemical reaction of nitration of

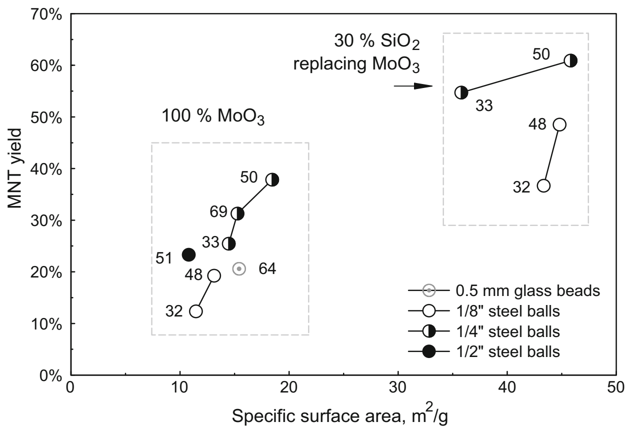

**Figure 8** Absolute MNT yield as a function of the surface area of the milled solids. Milling time is 2 h. Data point labels show effective milling temperatures in °C.

toluene is relatively complex. As with other mechanochemical reactions, one can initially assume that the reaction rate is proportional to the collision frequency of the milling media; it is further of interest to consider whether the energy dissipated in such collisions is affecting the reaction effectiveness or rate. Finally, it is of interest to consider how the temperature and catalyst properties affect the reaction.

The surface reaction expected for the mechanochemical nitration is supported by the relatively high p/o ratios obtained in this study and reported in Table 3. Indeed, liquid phase $H_2SO_4$ catalyzed nitration of toluene typically produces a mixture of 55–60% of ortho- or o-NT, 35–40% of para- or p-NT, and 3–4% of meta-, or m-NT [6]. Solid catalyzed surface reaction, on the other hand, typically leads to increased para-selectivity [6, 13, 14], as observed here.

To assess the effect of collision frequency on the reaction rate, consider the results with different milling media sizes shown in Fig. 2. A possible shift in the maximum yield of MNT to greater milling times for greater ball sizes supports the idea of reaction rate scaling with collision frequency, clearly increasing for smaller balls. At the same time, a reduced absolute maximum yield of MNT for 1/8″ steel balls compared to that for 1/4″ steel balls suggests that the energy dissipated in collisions affects the reaction effectiveness. The latter conclusion is also consistent with the results of experiments with glass beads. The number of collisions in such experiments is increased greatly; yet, the MNT yield is quite low, suggesting that the reaction is not occurring effectively at low energies dissipated in collisions.

It is tempting to assign significance to the optimized milling conditions, including milling time of 1 h (Fig. 2) and added 30% of fumed silica (Fig. 5) for the yield of MNT observed experimentally. However, the measurements showing the effects of time and silica addition represent both the reactions of formation of MNT and by-products and physical losses of the products, as emphasized by the reduced recovery rate seen in Figs. 3 and 6. For the effect of time, in particular (Fig. 3), yield of all by-products and recovery essentially follow each other after the maximum yield is achieved. Importantly, the toluene consumption continues to increase for longer milling times despite the reduced yield of all products. The product recovery reduced at greater milling times might be caused by greater adsorption of products to $MoO_3$ particles. The latter could be tentatively assigned to modification of $MoO_3$ surface by a greater number of collisions. Separating the effects of product recovery and optimized yield of MNT needs to be addressed in future work. For example, using solvents other than ethyl acetate employed in the present study may be considered. Alternatively, the reduced recovery rate could be related to secondary products that are not captured by the current extraction technique, such as gases caused by over-oxidation of any of the organic materials.

In case of added silica, the recovery improves with the silica fraction increasing above 70% (Fig. 6), while the MNT yield decays, clearly suggesting that it is $MoO_3$ and not $SiO_2$ that catalyzes the reaction. Additional experiments at shorter milling times as the most readily controlled experimental parameter may be needed to establish quantitative trends describing the MNT formation alone.

Although the MNT yield and product recovery correlate with each other for the experiments performed at different temperatures (Fig. 4), the yield of both dimers, important reaction by-products, follows a different trend. An increase in the production of dimers at elevated temperatures suggests a change in the reaction mechanism or an accelerated decomposition of the produced MNT, when the process temperatures are higher. These observations suggest that describing the present mechanochemical reaction theoretically would not be successful if only one global reaction, such as given by Eq. (1) is used. Additional reactions need to be included, which would account for either direct formation of by-products or for decomposition and oxidation of the generated MNT.

**Table 4** Selected surface area measurements and surface coverage estimates

| Ball diameter | Silica fraction (%) | SA ($m^2/g$) | Surface coverage with toluene monolayer (%) | MNT yield (%) | Surface coverage with MNT monolayer (%) |
|---|---|---|---|---|---|
| 1/8″ | 0 | 13.1 | 147 | 19.3 | 28 |
| 1/4″ | 0 | 18.4 | 104 | 37.9 | 39 |
| 1/8″ | 30 | 44.8 | 43 | 48.5 | 21 |
| 1/4″ | 30 | 45.8 | 42 | 60.9 | 25 |

Such additional reactions are also necessary to interpret the results shown in Fig. 6: at 90% of silica added, effectively no MNT was produced (less than 1%, Figs. 5, 6), while concentration of benzaldehyde was rather significant (more than 2%). Benzaldehyde, which is a typical product of oxidation of toluene [15, 16], is formed by direct oxidation of toluene in the presence of $NaNO_3$ and $MoO_3$.

To consider the effect of added silica on the MNT yield (Fig. 5), which is maximized when 30% of silica was added, one may need to account for the combined effect of the remaining catalyst ($MoO_3$) and an increased surface area of the solid caused by silica as milling aid. The increased surface area is expected to lead to a greater number of mechanically activated reaction events or greater overall reaction rate. The presence of $MoO_3$ should account for an effective formation of MNT once the reaction is mechanically activated. It is unlikely that adding relatively small amounts of silica affected significantly the rate of reaction because the peak of MNT yield was observed for the same fraction of silica replacing $MoO_3$ when different types of silica were used (Fig. 5), which were expected to produce different surface areas available for the reaction. The yield peaked at about 30% of added silica is likely associated with the specific $MoO_3/SiO_2$ ratio, which could affect catalytic activity of $MoO_3$, e.g., by altering a balance between Lewis and Brønsted acid sites in $MoO_3$ [17]. It was also reported that silica can interact with $MoO_3$ and improve its catalytic activity by forming polymolybdates [13]. Still, another possibility is that the added silica helps generating defects, serving as active sites on $MoO_3$. The effect of catalyst and its support requires further investigation, which can be warranted if the mechanochemical nitration of toluene is to be developed for practical applications.

A relationship between the observed MNT yield, possible reaction mechanism, and the surface area of the solids should also be briefly discussed. Table 4 shows selected surface area measurements for 1/8″ and 1/4″ steel balls with and without 30% silica, milled in the intermediate temperature regime at effectively 50.2 ± 1.7 °C. Taking the size of the toluene molecule as about 6 Å, derived from its molar volume, the corresponding coverage of the available surface with a toluene monolayer was estimated and is shown in Table 4. A similar estimate is made and shown for MNT as well. The available toluene, if spread uniformly across all solid surface, may form 1–2 monolayers in the cases without silica. It may only form a discontinuous monolayer in the case with silica. In both cases, the estimates suggest that the reaction occurs heterogeneously at the surface in a very thin liquid layer, with properties distinctly different from that of a bulk liquid. The data in Table 4 may also suggest that without silica, the available catalyst surface may be rate limiting, while the catalyst surface could be more effectively used with the high-surface area fumed silica added. Note that the formed MNT can only cover a fraction of the available surface and thus is unlikely to result in a substantial reduction in the available catalyst surface. Clearly, such assessments are approximate and combine the toluene present in the milling vial at the beginning of the run with the solid surface measured after the experiment. As the milling run progresses, the amount of toluene decreases. In runs without silica, the solid surface is expected to increase, at least initially; conversely, the surface is decreasing in time in runs with silica present. Despite the general decrease in the surface area in the latter case, the surface of composite $MoO_3/SiO_2$ particles acting as the catalyst must be increasing.

## Conclusions

It is observed that high practically significant yields of MNT are attainable by mechanochemical reaction of toluene and sodium nitrate with molybdenum oxide as a catalyst and without any added solvents. The reaction occurs with a high MNT yield when the ratio of liquid to solid is low, so that toluene is effectively spread in a monolayer on the surface of the catalyst. The rate of the mechanochemical nitration increases with the number of collisions; the reaction efficiency is also strongly affected by the energy dissipated in the collisions. Adding silica to the catalyst $MoO_3$ increases efficiency of the mechanochemical nitration of toluene as long as a sufficient amount of the catalyst remains available. The results suggest that introducing one global reaction may be inadequate for modeling mechanochemical nitration of toluene. Yields, which were optimized at a specific milling time and with specific silica content, will need to be described using additional reactions. Additional reactions are also necessary to describe the observed formation of by-products observed in the experiments, which were also affected by the milling temperature. At low concentrations of catalyst, direct oxidation of toluene by sodium nitrate can generate benzaldehyde, one of the main by-products. No evidence is found of formation of dimers, 2-methylphenyl-phenylmethanone and 4-methylphenyl-phenylmethanone, other significant by-products, by reactions directly involving toluene. Further work is needed to understand the reason for reduced yield and recovery at longer milling times; use of other solvents or other extraction techniques is necessary.

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