

Sulfated SO_4^{2-}/WO_3 as an efficient and eco-friendly catalyst for solvent-free liquid phase nitration of toluene with NO_2

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Abstract With the increase in environmental awareness, developing a highly efficient and environmentally benign nitration process has very important academic and applied industrial values in the synthesis of nitro-compounds. Towards this goal, we have developed an efficient and environmentally friendly approach for solvent-free liquid phase nitration of toluene by employing NO₂ as a nitrating agent and sulfated SO₄²⁻/WO₃ as a catalyst replacing traditional nitric acid–sulfuric acid under mild conditions. The results indicate that SO₄²⁻/WO₃ as an effective and eco-friendly catalyst exhibits excellent catalytic activity and reusability for the nitration of toluene with NO₂. In addition, the possible pathway for liquid phase nitration of toluene with NO₂ over sulfated SO₄²⁻/WO₃ catalyst was suggested. The present method makes this nitration process safe and environmentally friendly, and has the potential to enable a sustainable production of nitro-compounds from the liquid phase nitration of aromatic hydrocarbon with NO₂ in industrial applications.

Keywords Sulfated $SO_4^{2-}/WO_3 \cdot Nitrogen dioxide \cdot Mononitrotoluene \cdot Solvent-free \cdot Liquid phase nitration$

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Introduction

Nitration of aromatics is an industrially important reaction for the formation of many aromatic nitro compounds, which are versatile building blocks for the manufacture of various industrial products such as pharmaceuticals, dyes, explosives, pesticides, plastic, etc. [1–4]. Up to now, the industry has largely relied upon the classic technology for the production of nitro-aromatic compounds involving mixtures of nitric acid and sulfuric acid. The sulfuric acid plays a role in the formation of nitronium cations (NO₂⁺) by protonating nitric acid in this process. Despite the high efficiency, the mixed-acid process has some drawbacks, such as notorious corrosion, over-nitration and the generation of a large amount of corrosive spent acid and wastewater, which is environmentally unfriendly. Also, the separation of the products from the acids and the regeneration of the spent acid is quite cumbersome, expensive and energy intensive. The current environmentally economic considerations are increasingly unacceptable for this procedure. Therefore, there is an exigent need for developing more environmentally benign and economic nitration methods.

In recent years, with the increase in environmental awareness, chemical processes are facing challenges to reduce the use of environmentally hazardous chemicals. To this end, finding suitable solid acid catalysts to replace conventional liquid acid catalysts has been of great interest to researchers. Generally, in contrast to the conventional liquid acids, a solid acid catalyst has the advantages of a simple preparation method, being non-corrosive, with easy separation and being environmentally friendly. Hence, the nitration of aromatics by using solid acid catalysts instead of sulfuric acid is considered to be a promising alternative. Currently, several solid acid catalysts have been extensively explored for the liquid- or vaporphase nitration process, which mainly include $Cu_{1-x}Co_xFe_2O_4$ spinel ferrite [5] zeolite H-beta [6-11], MoO₃/SiO₂ [12-15], WO₃/SiO₂ [16], WO₃-TiO₂/SiO₂ [17], H₂SO₄/SiO₂ [18, 19], H₃PO₄/MoO₃/SiO₂ [20], sulfated zirconia [21], sulfated titania [22], sulfated SnO₂ [23], heteropolyacid [24–26], super-acidic metal oxides [27, 28], FeAAPILC [29], and modified TiO₂-ZrO₂ [30], etc. In the abovementioned nitration processes, a high concentration of nitric acid as the nitrating agent is still required for aromatics nitration whether vapor- or liquid-phase. Moreover, the regeneration of the resulting spent acid is not only expensive but also environmentally unsound in large-scale production. Therefore, some processes have been developed to reduce the spent acid generated by using different nitrating agents, like NO₂ [31–36], N₂O₄ [37], N₂O₅ [38, 39], nitrate salts [40], alkyl and acyl nitrates [31] as well as nitronium tetrafluoroborate [41]. From the point of view of being atom economic and environmentally benign, the direct employing of NO₂ (N₂O₄) as nitrating agent in place of nitric acid seems more attractive. First, a "neutral" reaction condition can provide a safe and non-corrosive operation. Second, the use of NO₂ can save costs in manufacturing the nitric acid. Therefore, the desirable nitration process for industry would be that NO₂ was directly used as the nitrating agent and solid acid as the catalyst, replacing nitric acid and sulfuric

acid, which can avoid the generation of large volumes of spent acid. Thus, it may be a promising alternative to the traditional mix-acid process.

In the past few decades, solfonated catalysts have been extensively used in several reactions because the catalyst is efficient [42–45]. However, few investigations on nitration reaction using solfonated catalysts has been so far reported. Here, we report a new environmentally friendly nitration method for toluene by employing NO₂ as the nitrating agent and sulfated SO₄²⁻/WO₃ as the catalyst (Scheme 1). The detailed results obtained from the catalytic nitration process will be reported here.

Experimental

Reagents and instruments

NO₂ (purity >99.9%) was purchased from the chemical reagent factory of Dalian, China. Toluene, ZrO₂, MoO₃, and SiO₂ were analytical grade and obtained commercially. Tungstic acid and ammonium metatungstate were purchased from Aladdin Industrial. Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus equipped with a hydrogen flame ion detector (FID) and a RTX[®]-5 (30 m × 0.25 mm × 0.25 um) column for quantitative analysis by using the internal standard method (chlorobenzene as the internal standard substance). Gas chromatography–mass spectrometry (GC–MS) was run on a Shimadzu GCMS-QP2010 Plus for qualitative analysis of products.

Preparation and characterization of the catalyst

Sulfated SO_4^{2-}/WO_3 catalyst was prepared by adopting a two-step route. In the first stage, the hydroxide gel contained W was obtained by precipitating a mixed solution of ammonium metatungstate with dilute aqueous ammonia solution (25%) under vigorous continuous stirring until the pH value was 9. Then, the obtained precipitate was filtered, washed until free of ammonium ions and dried at 373 K for 12 h. In the second stage, the resulting hydroxide gel was sulfated by 0.5 mol/L H₂SO₄ solution under ambient temperature (g/v = 1 g/5 ml), deposited overnight, dried at 373 K for 12 h and calcined at 773 K for 3 h in air. Finally, the SO_4^{2-}/WO_3 catalyst was obtained.

XRD patterns of the catalysts were examined by a Japan Rigaku D/Max-2550VB⁺ 18 KW X-ray diffractometer, using monochromatized CuK α radiation at a voltage and current of 40 kV and 300 mA. FT-IR spectra of samples were recorded using a Nicolet380 instrument in a KBr matrix in the range of

Scheme 1 Liquid-phase nitration of toluene with NO_2 over sulfated SO_4^{2-}/WO_3 catalyst



 $400-4000 \text{ cm}^{-1}$. Pyridine-adsorbed FT-IR was used to distinguish the nature of the acid sites. The images of the samples were characterized by SEM on a JSM-6360 electron microscope, and the morphology of the samples was recorded with TEM on a JEM-2100F with an accelerating voltage of 200 kV.

Typical experimental procedure

The nitration reaction of toluene with NO₂ was performed in a 100-ml stainless steel autoclave with a magnetic stirrer and temperature-controlling device. Typically, toluene (5 g), 0.3 g catalyst and a certain amount of cold liquid NO₂ (<5 °C, 7.5 g) were added together in an autoclave under low-temperature recirculation cooling conditions (remaining temperature 5–8 °C); NO₂ can be fully dissolved in toluene. Then, the sealed autoclave was immersed in an oil bath maintained at a set temperature. Finally, the reaction mixture was stirred at 70 °C for 6 h. The whole reaction system iswasclosed. After the reaction was finished, and the autoclave was cooled to room temperature, the catalyst was separated and recovered by filtration. The obtained products were analyzed by GC and GC–MS.

The GC operating conditions were as follows: the carrier gas was nitrogen; column model was RTX[®]-5 (30 m × 0.25 mm × 0.25 um); injector and detector temperatures were 310 °C; injected volume was 0.4 µL; split ratio was 1/40; and temperature program 110–230 °C at 30 °C/min and 230 °C for 5 min. The GC–MS operating conditions were the same as the GC operating conditions. The compounds were identified by comparing mass spectra with NIST08 and NIST08s library data. The separated components were determined by comparing the mass spectrogram of the standard compounds by computer and the relative content of each compound was obtained by peak area normalization.

Results and discussion

Comparison of catalytic performance of various catalysts in the nitration reaction of toluene with NO₂

In an attempt to seek a catalyst with an excellent performance for the liquid-phase nitration of toluene with NO₂, we screened several typical oxide catalysts. MoO₃ and WO₃ were chosen as representative acidic oxides, and ZrO₂ and SiO₂ were selected as weakly amphoteric and acidic oxides, respectively. Moreover, the prepared corresponding sulfated SO₄²⁻/MoO₃, SO₄²⁻/WO₃ and SO₄²⁻/ZrO₂ were also employed to catalyze the nitration of toluene with NO₂. Table 1 compares the catalytic performance of these oxides and sulfated catalysts in the nitration reaction. In the present reaction system, the products were mainly benzaldehyde (BAL), *ortho*-nitrotoluene (*n*-NT). Initially, nitration of toluene was carried out, as *p*-NT is commercially very important, and the research aim was to have maximum selectivity for *p*-NT and minimize the oxidation products. Therefore, the ratio of *o*-NT to *p*-NT (*o/p*) was considered as a key index to assess the reaction performance.

Catalyst	Conversion (%)	Selectivi	Selectivity (%)					
		BAL	o-NT	<i>m</i> -NT	<i>p</i> -NT			
None	14.2	28.6	36.3	9.0	26.1	1.40		
MoO ₃	27.4	33.4	37.5	2.6	26.5	1.42		
WO ₃	32.7	34.0	36.4	3.2	26.4	1.38		
ZrO ₂	31.6	32.5	39.3	2.1	26.0	1.51		
SiO ₂	28.3	30.2	38.1	7.5	24.2	1.57		
SO4 ²⁻ /MoO3	46.3	30.1	38.8	2.4	28.7	1.36		
SO4 ²⁻ /WO3	58.3	27.2	38.6	2.3	31.8	1.21		
SO4 ²⁻ /ZrO2	47.2	30.8	40.0	1.8	27.4	1.46		
SO4 ²⁻ /SiO2	48.0	29.6	35.4	9.8	25.2	1.41		

 $\label{eq:Table 1} \begin{array}{c} \mbox{Table 1} & \mbox{Comparison of the catalytic performance of various catalysts in the nitration reaction of toluene} \\ \mbox{with NO_2} \end{array}$

Reaction condition: temperature is 70 °C, time is 6 h, the molar ratio of toluene (5 g) to NO_2 is 1:2, and the amount of catalyst is 0.3 g

In the absence of any catalysts, the conversion of toluene was only 14.2% and the o/p ratio was 1.40. However, the conversion was improved by different extents as MoO₃, WO₃, ZrO₂ and SiO₂ were introduced to the nitration reaction. Among these oxides, the WO₃ catalyst exhibited better catalytic reactivity, and 32.7% of toluene conversion with 1.38 of o/p ratio was obtained. To our delight, the conversion and o/p ratio were remarkably boosted when the sulfated catalysts were introduced into this nitration reaction. Among these sulfated catalysts, the SO₄²⁻/WO₃ catalyst gave the higher results with 58.3% of toluene conversion and 1.21 of o/p ratio.

Characterizations of the WO₃ and SO₄²⁻/WO₃ samples

Figure 1 depicts the XRD patterns of the WO₃ and SO₄²⁻/WO₃ samples. As can be seen, both samples exhibit sharp peaks corresponding to the orthorhombic WO₃ phase at 2 θ values of 23.0, 23.4, 24.3, 26.5, 28.7, 33.3, 34.1 and 41.5° corresponding to (001), (020), (200), (120), (111), (021), (220) and (221) planes of orthorhombic crystalline WO₃ phase (JCPDS No. 20-1324), respectively. However, the characteristic peaks identified as the hexagonal structure of WO₃ with crystal planes of (200), (201), and (310) at 2 θ values of 27.6, 36.8 and 57.2° (JCPDS No. 33-1387), respectively, were not observed in the XRD patterns of the SO₄²⁻/WO₃ and WO₃ samples. Furthermore, no impurity existed in the WO₃ crystalline phase. It was noted that the degree of crystallinity of sulfated SO₄²⁻/WO₃ was relatively worse than that of WO₃.

Figure 2 shows the SEM and TEM micrographs of the WO₃ and SO₄²⁻/WO₃ samples. From the SEM images of the samples, it can be clearly seen that WO₃ displays the cube-like particles, while SO_4^{2-}/WO_3 looks like a fluffy snowball. Apparently, the degree of crystallinity of sulfated SO_4^{2-}/WO_3 seemed to be worse than that of WO₃. This result can also be seen from the XRD patterns of the WO₃





and SO_4^{2-}/WO_3 samples. In order to further obtain the insights on the interface of the samples and the crystal facet information (*d*-spacing) and size, the HRTEM images of the samples were adopted, as shown in Fig. 2. Two characteristic lattice fringes can be easily observed from the HRTEM images of the WO₃ and SO_4^{2-}/WO_3 samples. The fringes spacing of d = 0.386 nm was assigned to the (001) lattice plane, and the other fringes spacing of d = 0.261 nm was assigned to the (220) lattice plane. These studies confirm that the samples contain the orthorhombic crystalline WO₃ phase, which is in good agreement with the XRD characterization results.

In order to obtain information on the Brønsted and Lewis acidic sites of the catalysst, the distribution of the types of acidic sites on the catalysts is confirmed by FT-IR techniques using pyridine as a probe molecule. Figure 3 shows the FT-IR spectra of the adsorbed pyridine on the WO₃ and SO_4^{2-}/WO_3 samples in the 1400–1640 cm⁻¹ range. The band appearing at 1540 cm⁻¹ has been attributed to the adsorbed pyridine on the Brønsted acidic sites with the formation of pyridinum ions [23, 46, 47]. The bands appearing at 1450, 1505, 1558, 1575 and 1608 cm⁻¹ have been assigned to the adsorbed pyridine on the Lewis acidic sites [48, 49]. In addition, all the spectra exhibited bands at 1490 cm⁻¹ which are attributed to the adsorption of pyridine on the Brønsted and/or Lewis acidic sites [23, 49] or to the presence of adjacent Brønsted and Lewis acidic sites [50]. The possible reason is that the presence of a water or hydroxyl group on the surface of the catalysts gives weak Brønsted acidic sites, and the adsorption of water moleculse may convert Lewis acidic sites to weak Brønsted acidic sites. These results indicated that the WO₃ and sulfated SO₄²⁻/WO₃ samples exhibited strong Lewis acid sites and very weak Brønsted acidic sites.



Fig. 2 SEM and TEM micrographs of the samples: a WO_3 and b SO_4^{2-}/WO_3

Optimization of reaction conditions for the nitration of NO_2 with toluene over $SO_4{\,}^{2-}/WO_3$

The effects of different molar ratios of toluene to NO₂ on the conversion and selectivity over SO_4^{2-}/WO_3 were examined at 70 °C and the results are summarized in Fig. 4, which clearly shows that the conversion increased rapidly with the reduced molar ratio. Only 13.8% of conversion with 1.65 of *o/p* ratio was achieved at 1:0.5 of molar ratio of toluene to NO₂. Reducing the molar ratio to 1:3 led to a notable increase to 100% in the conversion and a gradual increase to 86.7% in the total selectivities for *o*-NT and *p*-NT with 1.12 of *o/p* ratio, while the selectivity to BAL decreased markedly. Meanwhile, a small amount of benzoic acid



Fig. 4 Catalytic performance of SO_4^{2-}/WO_3 in the nitration of toluene with NO_2 at different reaction conditions

(BAC) was formed, which showed that elevating the concentration of NO_2 was favorable for the nitration reaction of toluene with NO_2 to mononitrotoluene. However, further decreasing the molar ratio to 1:4, the selectivities of nitrotoluene

(*o*-NT and *p*-NT) showed a declining trend. This is due to the mononitrotoluene being further nitrated to dinitrotoluene at higher concentrations of NO₂. These results indicated that the molar ratio was a significant factor in regulating the product selectivities. From the indications of the selectivity of the the *p*-NT and the o/p ratio, the suitable molar ratio of toluene to NO₂ is 1:3.

Figure 4 also depicts the catalytic performance of the SO_4^{2-}/WO_3 catalyst for the liquid-phase nitration reaction at different reaction temperatures (40-90 °C). It was clearly found that there is a significant influence of reaction temperature on the conversion and selectivity. The conversion of toluene increased rapidly to 100%, while the selectivity to o-NT and p-NT first increased gradually then decreased with elevated temperatures, and the total selectivity of the nitration products reached 86.7%, and 1.12 of o/p ratio was obtained at 70 °C. However, the selectivity to BAL decreased with the elevated temperature. Interestingly, the formation of nitration products was favorable at temperatures lower than 70 °C, whereas further elevated temperatures (e.g., 90 °C) induced the oxidation reaction of toluene with NO₂ to BAL and BAC, which diminished the selectivity to the nitration products. This demonstrates that the active energy of the nitration reaction is higher than the oxidation reaction for forming BAL below 70 °C. In addition, the BAC product was detected as the reaction temperature was over 65 °C. Further increasing the reaction temperature to 90 °C, the oxidation reaction accelerated sharply, and the selectivity to BAC could reach 37.0%, while the total selectivities of the nitration products declined rapidly to 54.9%, which indicated that the oxidation ability of NO₂ was remarkably enhanced at the higher temperature (e.g., over 70 °C). These results demonstrated that the reaction temperature was a significant factor in regulating the product selectivity in the liquid-phase nitration of toluene and NO₂ over SO_4^{2-1} WO₃. From the indications of the o/p ratio, a favorable temperature should be selected at 70 °C.

In order to investigate the effects of reaction time on the nitration reaction, we tested the catalytic performance of SO_4^{2-}/WO_3 at different reaction times; the changes in the conversion and selectivity of the products with reaction time are shown in Fig. 4. As the time was prolonged from 1 to 6 h, the conversion significantly increased from 18.6 to 100%, the total selectivities to mononitroproducts gradually increased from 70.2 to 86.7% and the *o/p* ratio also slightly decreased from 1.26 to 1.12. However, the selectivity to BAL showed a declining trend with the reaction time, and the benzoic acid was evidently observed over 4 h. The possibility was that BAL was further oxidized to benzoic acid at the longer reaction time. Then, the selectivity to 8 h. Therefore, the appropriate reaction time was selected at 6 h.

In addition, the experimental results for the nitration reaction of toluene and NO₂ catalyzed by different amounts of SO_4^{2-}/WO_3 at 70 °C are listed in Fig. 4. Clearly, the conversion of toluene increased gradually, whereas the selectivity to the products and the o/p ratio were almost unchanged with the elevated amount of the catalyst. The conversion of toluene reached 100% with 86.7% of selectivity to nitrotoluene as 0.3 g of SO_4^{2-}/WO_3 was added to the nitration reaction, and a o/p ratio of 1.12 of was obtained. Therefore, a suitable amount of catalyst can

adequately and efficiently catalyze the nitration reaction of toluene with NO₂. The optimal amount of SO_4^{2-}/WO_3 was 0.3 g.

In summary, from the single factor experiment results, the optimal reaction conditions were obtained: that is, a molar ratio of toluene (5 g) to NO₂ of 1:3, a reaction temperature of 70 °C, a reaction time of 6 h, and an amount of the catalyst SO_4^{2-}/WO_3 of 0.3 g.

Comparison of catalytic performance and stability of sulfated SO_4^{2-}/WO_3 for the nitration of toluene in the NO₂ system and HNO₃ system

In order to investigate the catalytic performance and stability of sulfated SO_4^{2-}/WO_3 in the NO₂ or HNO₃ nitration system, the nitration reaction of toluene was performed in NO₂ and 65% of HNO₃, respectively, and the obtained results are summarized in Table 2. Clearly, the conversion of toluene was rapidly enhanced to 100% and the *o/p* ratio was remarkably improved as the sulfated SO_4^{2-}/WO_3 catalyst was introduced to the NO₂ or HNO₃ system. Furthermore, compared to the 98% H₂SO₄ catalyst, the *o/p* ratio given by sulfated SO_4^{2-}/WO_3 was evidently improved in the HNO₃ system. This demonstrates that the catalysis of sulfated SO_4^{2-}/WO_3 is very prominent whether in the NO₂ or the HNO₃ system.

In addition, for a heterogeneously catalyzed liquid-phase reaction, the catalyst recycling and durability has received considerable attention, in particular, for practical applications. In the present recycling tests, the sulfated SO_4^{2-}/WO_3 catalyst can be easily separated and recovered from the reaction mixture. In order to regenerate the catalyst, after 6 h of reaction, it was separated by filtration, washed with acetonitrile several times, dried at 100 °C and reused for the next run under the same conditions. In order to evaluate the efficiency and durability of the present catalyst, we have compared the results of catalyst reusability in the nitration of toluene with nitric acid and NO₂, respectively, as shown in Table 3. It ican bes clearly seen that the sulfated catalyst SO_4^{2-}/WO_3 kept up excellent catalytic activity in the first three recycles in the NO₂ system. A acceptable 80.4% of

Nitrating agent	Conversion (%)	Selectiv	Selectivity (%)						
		BAL	BAC	o-NT	<i>m</i> -NT	<i>p</i> -NT			
NO ₂	25.9	21.0	2.1	41.9	8.7	26.3	1.59		
NO ₂ ^a	100	11.6	1.7	44.9	1.8	40.0	1.12		
HNO ₃	18.3	_	_	65.3	2.7	32.0	2.04		
HNO ₃ ^a	100	_	_	56.8	4.3	38.9	1.46		
HNO ₃ ^b	100	-	-	60.5	3.0	36.5	1.66		

Table 2 Comparison of the nitration of toluene in different reaction conditions

Reaction condition: temperature, 70 °C, time, 6 h, toluene (5 g): $NO_2 = 1:3$ (molar ratio), toluene (5 g): HNO_3 (65%, 15.8 g) = 1:3 (molar ratio)

 a 0.3 g of SO₄²⁻/WO₃ catalyst was added

 $^{\rm b}$ 10.5 g of 98% ${\rm H_2SO_4}$ as catalyst was added in the absence of ${\rm SO_4}^{\rm 2-}/{\rm WO_3}$

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Recycle times	Conversion (%)	Select	$TOF^{a}(h^{-1})$						
		BEZ	BEA	o-NT	<i>m</i> -NT	<i>p</i> -NT	o/p	MNT	
1	100	11.6	1.7	44.9	1.8	40.0	1.12	86.7	9.06
2	100	10.8	2.5	45.4	2.0	39.3	1.15	86.7	9.06
3	95.1	12.1	2.7	43.1	2.0	40.1	1.08	85.2	8.61
4	87.5	12.6	2.0	43.9	1.8	39.7	1.10	85.4	7.93
5	80.4	12.3	2.1	43.7	1.9	39.9	1.10	85.6	7.28

Table 3 Catalytic recycling of SO_4^{2-}/WO_3 for the nitration of toluene in the NO₂ system

Reaction condition: temperature: 70 °C, time: 6 h, toluene (5 g): NO₂ = 1:3, catalyst: $SO_4^{2-}/WO_3 0.3$ g ^a TOF = (moles of toluene conversion)/(moles of W active site of the catalyst × reaction time)

conversion and 6.93 h⁻¹ of turnover frequency (TOF) were obtained after five runs. Moreover, whatever the recycling times, very steady selectivity was found. However, in the HNO₃ system, compared to the fresh catalyst, a substantial decrease in conversion from 100 to 63.2% and TOF from 9.06 to 2.04 h⁻¹ were observed in the second runs as shown in Table 4. After five runs, only 22.5% of toluene conversion was achieved. In addition, the *o/p* ratio was obviously lower in the NO₂ system compared with that in the HNO₃ system. These results show that the sulfated SO_4^{2-}/WO_3 exhibits a good catalytic performance and durability in the NO₂ system.

The reused catalyst in the NO₂ system was characterized by several techniques such as SEM, TEM and XRD. Figure 5a, b gives the SEM images and TEM images of the fresh and used SO_4^{2-}/WO_3 catalyst after five cycles. The morphology of the catalyst was not notably changed, as can be seen from the images. Figure 5c compares the XRD pattern of the fresh SO_4^{2-}/WO_3 catalyst with that of the catalyst after being used five times. The XRD patterns of the virgin and used catalysts were nearly the same, indicating that the crystal structure of the catalysts was unchanged in the reaction.

Recycle times	Conversion (%)	Selectivi	Selectivity (%)					
		o-NT	<i>m</i> -NT	<i>p</i> -NT	o/p			
1	100	56.8	4.3	38.9	1.46	9.06		
2	63.2	57.0	4.2	38.8	1.47	5.72		
3	45.8	56.5	4.4	39.1	1.45	4.15		
4	32.7	56.7	4.3	39.0	1.45	2.96		
5	22.5	56.4	4.5	39.1	1.44	2.04		

Table 4 Catalytic recycling of SO₄²⁻/WO₃ for the nitration of toluene in the HNO₃ system

Reaction condition: temperature: 70 °C, time: 6 h, toluene (5 g): HNO₃ (65%, 15.80 g) = 1:3, catalyst: $SO_4^{2-}/WO_3 0.3 g$



Fig. 5 SEM images (a), TEM images (b) and XRD patterns (c) of the fresh and used ${\rm SO_4}^{2-}/{\rm WO_3}$ catalyst



Fig. 6 Possible reaction pathway of toluene with NO₂ over sulfated SO_4^{2-}/WO_3

The possible reaction pathway of toluene with NO₂ over sulfated SO_4^{2-}/WO_3

Generally, the reaction mechanism for the liquid-phase nitration of aromatic hydrocarbon over a solid-acid catalyst has been regarded as an electrophilic attack mechanism [36, 51]. Based on the experimental results and literature reports, the possible reaction pathway for the catalytic nitration of toluene with NO₂ over the

 SO_4^{2-}/WO_3 catalyst is suggested in Fig. 6. In the present sulfated catalyst SO_4^{2-}/WO_3 , it is evident that the acidity site is present on the metal W centre. Firstly, the water molecule can be polarized on the W site for generating the Brønsted acidity. The acidic H⁺ of polarized water can react with liquid NO₂ (N₂O₄) to form nitronium ions (NO₂⁺) with nitrous acid (HNO₂) as a by-product. The formed NO₂⁺ easily attacks the aromatic ring by an electrophilic reaction. Then, the aromatic hydrocarbon was subsequently converted to a nitro-product. Meanwhile, the generated HNO₂ was easy to decompose to NO, NO₂ and water. It is noted that the aromatic hydrocarbon may not require to be activated at the catalyst surface in this nitration process. In the present study, the formation of just a mononitro-product was observed without any dinitro-product formation.

Conclusions

In conclusion, we have developed an environmentally benign process for the nitration of toluene by using NO₂ as the nitrating agent and sulfated SO_4^{2-}/WO_3 as the catalyst. The optimized reaction conditions were obtained. The results indicated the nitration gave excellent toluene conversion (100%) with good mono-nitration selectivity and *o/p* ratio under suitable conditions. Compared to the conventional nitration process, there was no other organic solvent or sulfuric acid used in the reaction system, which made it more environmentally friendly. Moreover, the present sulfated catalyst SO_4^{2-}/WO_3 has been proven to have excellent catalytic activity and stability in the NO₂ nitration process. In addition, the possible reaction pathway of toluene with NO₂ over sulfated SO_4^{2-}/WO_3 was suggested. This work provides a versatile selective method for the preparation of nitro-aromatic compounds, and has very important academic and applied industrial values.

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