Heterogeneous Reactions between Toluene and NO₂ on Mineral Particles under Simulated Atmospheric Conditions

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Supporting Information

ABSTRACT: Heterogeneous reactions between organic and inorganic gases with aerosols are important for the study of smog occurrence and development. In this study, heterogeneous reactions between toluene and NO₂ with three atmospheric mineral particles in the presence or absence of UV light were investigated. The three mineral particles were SiO₂, α-Fe₂O₃, and BS (butlerite and szmolnokite). In a dark environment, benzaldehyde was produced on α-Fe₂O₃. For BS, nitrotoluene and benzaldehyde were obtained. No aromatic products were produced in the absence of NO₂ in the system. In the presence of UV irradiation, benzaldehyde was detected on the SiO₂ surface. Identical products were produced in the presence and absence of UV light over α-Fe₂O₃ and BS. UV light promoted nitrite to nitrate on mineral particles surface. On the basis of the X-ray photoelectron spectroscopy (XPS) results, a portion of BS was reduced from Fe³⁺ to Fe²⁺ with the adsorption of toluene or the reaction with toluene and NO₂. Sulfate may play a key role in the generation of nitrotoluene on BS particles. From this research, the heterogeneous reactions between organic and inorganic gases with aerosols that occur during smog events will be better understood.

INTRODUCTION

Heterogeneous reactions in the atmosphere play a major role in transforming gases and determining the compositions of the atmosphere.¹ During smog formation, heterogeneous and homogeneous reactions among particles, as well as natural and anthropogenic gases, are the main contributors to the polluted air.² Recent studies of heterogeneous reactions have focused on single organic or inorganic gases with aerosol particles.^{3–5} However, the atmospheric environment is a mixed gas system, and irradiation effects need to be considered for heterogeneous reactions.

Toluene is a ubiquitous environmental pollutant that can be both biogenic and anthropogenic. Sources of anthropogenic toluene include industrial emissions, indoor air, and exhaust from motor vehicles.⁶ Toluene is the most abundant aromatic compound in urban atmospheres⁷ and accounts for approximately 20–40% of total aromatic volatile organic compounds (VOCs).⁸ Toluene and its derivatives, such as benzaldehyde and nitrotoluene, have received considerable attention due to their adverse effects on both the environment and human health.^{9–14} Some of these compounds are mutagenic,^{15,16} carcinogenic,^{17,18} or otherwise toxic to aquatic^{19,20} and terrestrial organisms.^{21,22} Therefore, the formation of nitrotoluene and benzaldehyde in the atmosphere must be investigated.

The emission of benzaldehyde in atmosphere has been attributed to biogenic emissions, photochemical reactions, and anthropogenic emissions.^{23–25} Benzaldehyde is produced in the atmosphere via complex reactions between toluene, hydroxyl radicals, and NO_x involving both heterogeneous and homogeneous reactions.^{26,27} In contrast, the emission of nitrotoluene in the atmosphere is almost exclusively anthropogenic, primarily from the incomplete combustion of fossil fuels and industrial processes.²⁸ Nitrotoluene can also be formed from natural atmospheric homogeneous reactions; toluene reacts with the OH radical to form an OH-monocyclic aromatic adduct that reacts with O₂ and NO₂ to form 3-nitrotoluene.²⁶ However, studies of the formation of nitrotoluene via atmospheric heterogeneous reactions have been limited.

Mineral aerosols originate from soil particles that have been entrained by strong wind currents and enter the atmosphere.²⁹ The chemical composition of mineral aerosols is similar to that of crustal rocks, which are dominated by SiO₂, Al₂O₃, and Fe₂O₃.³⁰ Furthermore, iron and sulfate ions are the most prevalent transition metal and ion, respectively, in atmospheric

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Table 1. Assignment of Vibrational Bands (cm^{-1}) of Surface Species Formed when Mineral Particles Were Exposed to NO_2 , Toluene or NO_2 , and Toluene

surface species	gas	in this work						in lit.
		SiO ₂		α-Fe ₂ O ₃		BS		
		dark	UV	dark	UV	dark	UV	
bidentate nitrito*	NO ₂			1221	1219			1210, ³² 1220–1205 ³²
	NO ₂ + toluene			1210	1216			
monodentate nitrate*	NO ₂		1558	1556, 1270	1554, 1271			1556, ³² 1275 ³² 1547 ⁴³ 1545, ⁶⁷ 1276 ⁶⁷
	NO ₂ + toluene			1559	1557			
bidentate nitrate*	NO ₂					1575	1575	1582 ³²
	NO ₂ + toluene		1585			1580	1578	1588 ⁴³ 1581 ⁶⁷
bridging nitrate*	NO ₂			1616, 1603	1613, 1606	1621, 1608	1621, 1607	1615 ³² 1628 ⁴³ 1603 ⁶⁷
	NO ₂ + toluene			1616, 1603	1620, 1603	1621, 1603	1623	
nitric acid (HNO ₃)	NO ₂			1337, 1296	1339, 1297			1677, ⁴¹ 1399, ⁴¹ 1315, ⁴¹ 1338 ⁴³
	NO ₂ + toluene	1676	1658	1336, 1290	1336, 1297			1710, ⁶⁶ 1320 ⁶⁶
adsorbed NO	NO ₂			1809, 1790	1809, 1790	1809, 1790	1809, 1790	1807, ⁵¹ 1788 ⁵¹
	NO ₂ + toluene		1808, 1790		1809, 1790			
adsorbed N ₂ O ₃ or Fe ^{III} –NO	NO ₂					1888	1880	1880 ⁵⁰
	NO ₂ + toluene					1884	1885	
adsorbed N ₂ O ₄	NO ₂		1731, 1716					1748–1740, ⁴² 1710 ⁴² 1749 ³
	NO ₂ + toluene			1758				
NO ⁺ or NO ₂ ⁺	NO ₂					2098	2094	2290–2102 ⁴²
	NO ₂ + toluene					2098	2099	
aromatic ring, methyl and methyleneν(C–H)	toluene	3087, 3063, 3031, 2929, 2880	3089, 3064, 3032, 2930, 2883	3082, 3031, 2927, 2880, 2835	3085, 3057, 3028, 2953, 2930, 2877	3086, 3060, 3032, 2931, 2880	3091, 3066, 3033, 2927, 2880	3075, ³⁸ 3033, ³⁸ 2932, ³⁸ 2877 ³⁸ 3072, ⁶⁸ 2740, ⁶⁸ 2956 ⁶⁸ ⁶⁵ 3086, ⁶ 3062, ⁶ 3031, ⁶ 2928, ⁶ 2880 ⁶
	NO ₂ + toluene	3085, 3068, 3029, 2931, 2880	3088, 3071, 3038, 2929, 2876, 2837, 2761	3085, 3065, 3028, 2996, 2949, 2922, 2883	3075, 3031, 2983, 2949, 2878	3069, 3030, 2967, 2926, 2880	3047, 3035, 2994, 2938, 2885	
skeletal ν(C–C)	toluene	1602, 1496	1603, 1496	1602, 1496	1602, 1496	1602, 1496	1602, 1496	1596, ³⁸ 1501 ³⁸
	NO ₂ + toluene	1603, 1496	1600, 1496	1603, 1496	1603, 1496	1603, 1496	1598, 1496	
ν(C=O)	NO ₂ + toluene		1700, 1685	1699, 1678, 1654	1699, 1687, 1658	1671	1687	1694–1629, ³⁸ 1689, ⁶ 1682, ¹¹ 1680 ⁶⁹
ν(C–N)	NO ₂ + toluene					1521	1523

Figure 1. In situ DRIFTS spectra of SiO₂ (a1 and a2), α -Fe₂O₃ (b1 and b2) and BS (c1 and c2) as a function of time in a flow of 47 ppm of NO₂ in the absence and presence of UV irradiation, respectively. Note: Each group of spectra was collected at its respective background baseline. The baseline intensity did not change with time. The offset was applied only for a clear view both for Figures 1 and 2.

aerosols.² NO₂ is one of the major gaseous pollutants in vehicle exhaust. Therefore, mineral aerosols, NO₂, and toluene are ubiquitous in ambient air. Recent studies have examined heterogeneous reactions of NO₂ and mineral particles.^{31–34} These studies have focused on different products, such as nitrite and nitrate, on the mineral particle surface. However, few studies were carried out to investigate mixtures of gases, especially mixtures of inorganic and organic gases.^{35,36} In these few studies, the effects of NO₂ and toluene on magnetite have indicated that NO₂ and water decrease the adsorption of toluene. In this study, SiO₂, α -Fe₂O₃, and iron sulfate were selected as model mineral particles to investigate the effects of heterogeneous reactions of toluene and NO₂ on these substrates. This research will facilitate the elucidation of the chemical behavior and heterogeneous reactions of toluene as well as the sources of nitrotoluene and benzaldehyde in the atmosphere, under dark or UV light conditions. In this work, several in situ experiments were designed to investigate the chemical reactions between toluene and NO₂ with mineral particles. UV light was used to simulate daytime sunlight. The mineral particles were examined by XPS to detect the changes on particle surfaces.

MATERIALS AND METHODS

The three mineral particles' physical characterization, chemicals used in this study, and the particle pretreatment procedure are shown in the [Supporting Information](#).

Reaction Procedure and Analytical Methods. All experiments were performed at 305–306 K. Infrared spectra of solid samples were recorded on a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700; Thermo Fisher) equipped with a mercury cadmium telluride (MCT) detector. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were recorded in the spectral range from 4000 to 650 cm⁻¹ at a resolution of 4 cm⁻¹, and in general, 32 scans

were performed during the experiments. The mass of each particle was around 0.05 g. The powder particle was placed in a Harrick IR reactor. The reactor was sealed with a dome. All gases were fully mixed before direct introduction into the reactor. The details of the procedure are similar to those used in a previous study.³⁷ When toluene and NO₂ were mixed with air, the ranges of toluene and NO₂ were 160 ± 3 and 40 ± 3 ppm, respectively. When toluene or NO₂ was mixed with air, the ranges of toluene and NO₂ were 166 ± 3 and 47 ± 3 ppm, respectively. GC–MS was not coupled with DRIFTS. After DRIFTS experiments, each sample was transferred to a headspace bottle with an aluminum lid with a rubber pad. The lid was sealed with a cap. Then the sealed sample was analyzed by gas chromatography–mass spectrometry (GC–MS; QP2010Plus, Shimadzu) on an instrument equipped with an automated headspace sampler (PE HS 40, PerkinElmer). A 2 m path length gas cell (Thermo Fisher) was used to investigate the homogeneous reactions of toluene and NO₂ on dark and UV conditions.

For the experiments with UV light, the irradiation was supplied by a xenon lamp (500 W) with continuous emission in the 300–400 nm range through the dome window. The spectrum of the Xe lamp is shown in [Figure S1](#). An optical fiber was used to transmit the light from the xenon lamp (Aulight, Beijing).

RESULTS AND DISCUSSION

Characteristics of Mineral Particles. The pretreated α -Fe₂O₃ and FeSO₄·7H₂O samples were characterized by XRD. On the basis of the XRD patterns ([Figure S2](#)), FeSO₄·7H₂O was identified as Fe(SO₄)(OH)·2(H₂O) (butlerite, PDF 71–2397) and FeSO₄·H₂O (szmolnokite, PDF 81–0019). In this study, BS was used to represent the pretreated products of FeSO₄·7H₂O. α -Fe₂O₃ was confirmed as hematite. The physical properties for all mineral particles are listed in [Table S1](#). From

Figure 2. In situ DRIFTS spectra of SiO₂ (a1 and a2), α -Fe₂O₃ (b1 and b2), and BS (c1 and c2) as a function of time in a flow of 40 ppm of NO₂ and 160 ppm toluene in the absence and presence of UV irradiation, respectively.

the SEM observation results (Figure S3), hematite was nearly spherical, and BS and SiO₂ were amorphous.

In Situ DRIFTS Study. To investigate the heterogeneous reactions of toluene and NO₂ with mineral particles, in situ DRIFTS experiments were performed in a selective flow system. The detailed assignment of the vibrational bands of the surface species that formed when samples were exposed to NO₂, toluene, or both is provided in Table 1. The geometries of surface species were demonstrated in Figure S4. The detailed infrared spectra of the SiO₂, α -Fe₂O₃, and BS particles in flows of NO₂, toluene, and both gases with synthetic air under dark or UV light conditions are shown in Figures 1 and 2 and Figure S5. For the homogeneous reactions, based on the 2 m path length gas cell, it was different when new aromatic products were detected (Figure S5). The DRIFTS spectra results for SiO₂, α -Fe₂O₃, and BS exposed to toluene are shown in Figure S6. At room temperature, toluene interacted weakly with SiO₂, as indicated by the disappearance of the peak at 3741 cm⁻¹ and the appearance of a peak at 3614 cm⁻¹. The latter band indicated the preferential adsorption of toluene on isolated hydroxyl groups present on the surface of the material. Furthermore, the peaks at 3276 and 1621 cm⁻¹ weakened with increasing exposure time, indicating that toluene displaced some water molecules on the surface of SiO₂. This phenomenon was also observed on the surface of α -Fe₂O₃ and BS (Figure S6b,c). In the C–H stretching region (3100–2850 cm⁻¹), peaks at 3087, 3063, 3031, 2929, and 2880 cm⁻¹ were observed (Figure S6a). The first three peaks were assigned to the C–H stretching vibrational band of the aromatic rings. The latter two peaks were assigned to the C–H asymmetric stretching of methylene and symmetric stretching of methyl.^{38–40} This result indicates that hydrogen– π bonding of toluene is preferred over H bonding between its methyl group and –OH surface groups. The peaks at 1602 and 1496 cm⁻¹ correspond to the stretching vibrational and out-of-plane

bending vibrational bands of C–H bonds, respectively.³⁸ However, no new aromatic product was observed (Figure S6a).

The infrared spectra of SiO₂ particles with NO₂ in the absence and presence of UV are shown in Figure 1a1 and Figure 1a2. In a flow of NO₂ without UV light, the peaks at 1676 and 1620 cm⁻¹ were predominant, indicating adsorbed nitric acid and bridging nitrate or water, respectively (Figure 1a1). In previous studies, the peaks at 1628 and 1602 cm⁻¹ were assigned to gas-phase NO₂.⁴¹ The broad band at 1620 cm⁻¹ may overlap with the adsorbed gaseous NO₂ band. Therefore, the peak at 1620 cm⁻¹ did not have a definite conclusion. Compared with the results observed under dark conditions, several peaks appeared upon UV irradiation (Figure 1a2). The peaks at 1731 and 1716 cm⁻¹ can be attributed to adsorbed N₂O₄.⁴² The peak at 1804 cm⁻¹ may be from a surface dinitrosyl complex.⁴² The peak at 1669 cm⁻¹ was assigned to nitric acid.⁴² For SiO₂, the UV irradiation promoted N₂O₄ generation on particles (Figure 1a2).

When toluene was added to the flow with NO₂ in the dark environment, no new peaks were observed (Figure 2a1). In contrast, with UV irradiation, new peaks were observed at 1700 and 1685 cm⁻¹, indicating the formation of benzaldehyde (Figure 2a2), which was confirmed by the GC–MS results. The peaks observed at 1808 and 1790 cm⁻¹ corresponded to adsorbed NO (Figure 2a2).⁴³

The heterogeneous reactions of α -Fe₂O₃ with NO₂ in either the presence or absence of UV light were similar (Figure 1b1 and b2). During the dark experiment, the peaks at 1080 and 1221 cm⁻¹ were assigned to nitrite products. These peaks appeared first and decreased with exposure time. In contrast, the peaks at approximately 1622 cm⁻¹, which were assigned to bridging nitrate, strengthened with exposure time. Then, monodentate nitrate bands were observed as peaks at 1270 cm⁻¹.³² The peaks at 1297 and 1337 cm⁻¹ rapidly increased and acted as the dominant nitrate on the α -Fe₂O₃ surface. These two peaks were due to nitric acid.⁴⁴ On the basis of these

results, the reaction between $\alpha\text{-Fe}_2\text{O}_3$ and NO_2 was attributed to the conversion of the nitrite to nitrate, and the final stable product was nitric acid (Figure 1b1). The peaks at 1809 and 1790 cm^{-1} assigned to adsorbed NO were observed in both the presence and the absence of UV irradiation (not demonstrated in the figures). With respect to the NO_2 and toluene gaseous mixture group, the peak at 1758 cm^{-1} was assigned to adsorbed N_2O_4 because NO_2 molecules tend to dimerize at low temperatures (Figure 2b1).⁴² Previous studies have confirmed that the peaks ca. 1745 and 1710 cm^{-1} correspond to adsorbed N_2O_4 .^{45,46} The peaks at 1699, 1678, and 1654 cm^{-1} , which are relatively large, indicate the presence of different types of adsorbed benzaldehyde with carbonyl groups that interact with surface Lewis acid sites on the $\alpha\text{-Fe}_2\text{O}_3$ surface (Figure 2b1).^{47–49} The peaks at 1699, 1687, and 1658 cm^{-1} were assigned to the carbonyl stretching vibration of benzaldehyde for the UV irradiation experiments (Figure 2b2).

The peaks resulting from the heterogeneous reaction of NO_2 and BS are listed in Table 1. The peak at 2098 cm^{-1} corresponds to NO^+ or NO_2^+ , which is not yet confirmed (Figure 1c1).⁵⁰ This band was only observed for the BS group. This result indicated that the sulfate ion may enhance the yield of NO^+ or NO_2^+ . Bidentate nitrate and bridging nitrate were detected, and their intensities increased during the process. The peak at 1888 cm^{-1} (Figure 1c1) was assigned to the $\text{Fe}^{n+}\text{-NO}$ band or attributed to adsorbed N_2O_3 .⁵¹ However, the peak was observed during the first 5 min, and its intensity then weakened and ultimately disappeared. Therefore, the peak at 1888 cm^{-1} may be due to adsorbed N_2O_3 . In contrast, the intensities of the peaks at 1809 and 1790 cm^{-1} , which correspond to adsorbed NO complexes on the Fe^{3+} site, increased during the experiment.⁴³ The two peaks immediately disappeared when the supply of NO_2 was cut off and air purged the BS particle for 5 min (Figure 1c1). However, the peak at 2098 cm^{-1} did not disappear within 20 min after ceasing the injection of NO_2 into the system (data not shown). The peak at 1880 cm^{-1} appeared after more than 10 min under UV light irradiation (Figure 1c2), in contrast to its appearance after only 2 min under dark conditions (Figure 1c1). These results suggest that irradiation with 300–400 nm light favors the formation of N_2O_3 , which is consistent with a previous report.⁵² In the NO_2 and toluene group, the band at 1671 cm^{-1} corresponded to the carbonyl ($\text{C}=\text{O}$) stretching vibration of benzaldehyde (Figure 2c1). The peak observed at 1521 cm^{-1} was assigned to the asymmetric stretching vibrational band of $\text{C}-\text{N}$. This result was confirmed by the following GC-MS analysis. As shown in Figure 3a, peaks were observed in the total ion chromatogram (TIC) of the products for the heterogeneous reaction between toluene and NO_2 on BS particles with UV irradiation. The four peaks were identified as benzaldehyde, 2-nitrotoluene, 3-nitrotoluene, and 4-nitrotoluene, and these results were confirmed based on the spectra of standard samples. The results indicated that all of the nitrotoluene isomers were detected.

The peaks at 1809 and 1790 cm^{-1} were not observed in the $\alpha\text{-Fe}_2\text{O}_3$ (Figure 2b1) and BS (Figure 2c1) experiments, in contrast to the experiment with only NO_2 (Figure 1b1 and c1), possibly due to toluene competing with NO_2 for the Fe^{3+} site. This result indicates that toluene is more reactive than NO_2 in this study. Other studies have suggested that toluene is more reactive and competes with NO_2 on oxidized magnetite particles, whereas NO_2 is more reactive on reduced magnetite.³⁶

Figure 3. Products of the heterogeneous reaction of toluene with NO_2 on the surface of BS with UV irradiation (a) and the integrated areas of TICs for different products on the three particles under 40 ppm of NO_2 and 160 ppm toluene in the presence or absence of UV light (b).

This result implied that nitrotoluene could be produced in the atmosphere under suitable conditions. Sulfur dioxide (SO_2) and $\alpha\text{-Fe}_2\text{O}_3$ are a common air pollution gas and a common mineral particle, respectively. Sulfuric acid can be produced from the reaction of SO_2 with water. Therefore, heterogeneous reactions among SO_2 , NO_x , water, and iron particles (BS in this study) could lead to the formation of more toxic nitrotoluene products. The results suggest that the source of nitrotoluene in the atmosphere is from both direct anthropogenic emissions and secondary organic aerosols (SOAs) generated from heterogeneous reactions between aromatic compounds, NO_2 , and particulate matter. These SOAs that contribute to smog are less volatile than the gas (toluene) originally emitted.⁵³ Experiments conducted under dark conditions confirmed that nitrotoluene and benzaldehyde can be generated during the night on BS particles. It should be noted that toluene and NO_2 do not react under dark conditions on SiO_2 particles (Figure 2a1); i.e., both toluene and NO_2 are stable when mixed in the gas phase in dark conditions. Therefore, in this study, heterogeneous reactions promote the oxidation of toluene to benzaldehyde. Importantly, exposure of toluene to the three types of particles under irradiation did not result in the formation of new products in the absence of NO_2 . This result indicates that NO_2 significantly influences the heterogeneous reaction for the generation of benzaldehyde and nitrotoluene during the day and night.

Effects of UV Irradiation. From the DRIFTS results (Figure 1b2), the peaks at 1082 and 1219 cm^{-1} vanished quickly when UV light was applied to the reaction between $\alpha\text{-Fe}_2\text{O}_3$ and NO_2 . This result suggests that UV light promotes the transformation from nitrite to nitrate. This conclusion was also verified by XPS results (Figure S7). The binding energy of the peak at approximately 407 eV was assigned to NO_3^- .⁵⁴ The intensity of nitrate generated from the UV experiment is 48 times larger than that from the dark experiment through a normalization calculation. UV light increases the number of defect sites carrying negative charges on the $\alpha\text{-Fe}_2\text{O}_3$ surface by increasing the amount of nitrate species on the surface.⁵⁴ It

Figure 4. Fe 2p and Fe 3p XPS spectra of fractions from α -Fe₂O₃ (a1 and a2) and BS (b1 and b2) in dark experiments.

should be noted that for the BS group nitrate was only observed in the UV experiment. Note that the peaks at approximately 401.8 and 400.0 eV have yet to receive a definite assignment. Some of the previous studies considered these peaks as two different NO⁺ species.⁵⁵ Other studies assigned them to NO[−] and nitrogen species at defects.⁵⁶ In addition, for the BS particle exposed to NO₂, the integrated area ratio of bidentate nitrate to bridging nitrate under UV light conditions was always higher (20–44%) than the ratio under dark conditions (Figure S8). With irradiation, bidentate nitrate, which is more stable than bridging nitrate, was promoted on the BS surface. Therefore, the irradiation of UV promoted the reaction on BS particles.

To analyze the chemical composition of the surface of α -Fe₂O₃ and BS particles exposed to toluene or toluene and NO₂, the high-resolution spectra XPS of O 1s, Fe 2p, and Fe 3p were collected. For α -Fe₂O₃, the O 1s spectra were fitted with 529.4, 531.1–531.2, 532.6 ± 0.3 eV, which were assigned to the main oxide O–Fe, lattice FeOH and/or O=C, and O–C and/or adsorbed water, respectively.^{57–59} The peak around 532.5 eV could be the O–N (nitrate).⁶⁰ For the BS particle, O 1s spectra were fitted with one more peak at 532.2 eV (O=S).⁶¹ In Table S1, the ratio of adsorbed oxygen/lattice oxygen (AO/LO) was calculated on the basis of the fitted areas of different O 1s species. With respect to the XPS O 1s spectra, an increase in the ratio of adsorbed oxygen/lattice oxygen (AO/LO) was observed for both α -Fe₂O₃ and BS samples exposed to toluene alone under dark conditions, as shown in Table S1. For α -Fe₂O₃, the ratio change is close to the uncertainty limits, so a definite mechanism cannot be confirmed at this stage. For BS particles, the increase of the AO/LO ratio appears to occur at the expense of the oxide, suggesting that toluene interacts with the oxygen from the oxide.³⁶ In contrast, the ratio of AO/LO increased dramatically for toluene adsorbed on α -Fe₂O₃ in the UV group (Table S2). However, the ratio was similar when comparing the results in the absence and presence of UV for the BS group, which indicates that UV irradiation promotes the formation of adsorbed oxygen on the α -Fe₂O₃ surface instead of that on the BS particles. The increase in adsorbed oxygen

may arise from surface hydroxyl and not from C=O (Figure S9d). GC–MS analysis did not indicate the formation of new products from the reaction of toluene and α -Fe₂O₃ under UV irradiation.

From the DRIFTS results, the integrated areas of the peaks at 3099–2991 and 2991–2846 cm^{−1} or 3099–2993 and 2989–2784 cm^{−1} are shown in Figure S10. The former represents the aromatic ring (AR) C–H, and the latter represents the C–H symmetric and asymmetric vibration of methyl and methylene (MM). These two parameters suggest that toluene has been adsorbed on the substrates. For the dark experiment, the changes in AR and MM were similar, and the adsorption of toluene reached a stable state after 40 min. However, in the irradiation experiment, the intensities of the AR and MM bands reached equilibrium in 200 min. This result may indicate that the adsorption pattern of toluene on the α -Fe₂O₃ surface is different when in the presence of UV light.

The integrated areas of TICs for different products on the three mineral particles with NO₂ and toluene under dark and UV light conditions are shown in Figure 3b. UV light dramatically stimulated the formation of benzaldehyde on iron particles. Approximately 2.5 and 7.7 times more benzaldehyde was produced under UV light compared to the dark experiment on α -Fe₂O₃ and BS particles, respectively. For nitrotoluene, the promotive effect of UV was reasonable. In previous studies, 3-nitrotoluene has been detected due to homogeneous reactions between OH radicals, aromatic compounds and NO_x.²⁶ It should be noted that the benzaldehyde quantity on SiO₂ is slightly greater than that on BS, which indicates that part of the benzaldehyde may be produced in the gas phase. In the gas phase, benzyl was generated by the UV irradiation of toluene. Benzaldehyde was produced from the reactions between benzyl and N_xO_y. Benzaldehyde was then adsorbed on particle surfaces and detected by FTIR. This requires further investigation. The benzaldehyde amount on α -Fe₂O₃ was less compared to that on BS particles under UV light. This probably occurs because UV light promotes the production of nitrate from NO₂ on α -Fe₂O₃

surfaces and nitrate did not participate in benzaldehyde formation (Figure S11).

The temporal changes in the integrated areas of benzaldehyde are presented in Figure S12. For the dark experiment, the peaks at 1699, 1678, and 1654 cm^{-1} were assigned to C=O stretching of benzaldehyde (Figure S12a). For the irradiation experiment, the peaks at 1699, 1687, and 1658 cm^{-1} correspond to the carbonyl stretching vibration of benzaldehyde (Figure S12b). The integrated area continuously increased with time under dark conditions. The amount reached a maximum after 90 min and desorbed gradually with time. In contrast, in the irradiated groups, the integrated area and the benzaldehyde amount increased during irradiation time.

Discussion of the Heterogeneous Reactions. In the absence of UV irradiation, no new aromatic products were detected on SiO_2 , even in the presence of NO_2 and toluene. This suggested that toluene and NO_2 could not react in the gas phase during nighttime. However, with the participation of iron compounds, heterogeneous reaction products were observed. Toluene reacts with NO_2 to produce benzaldehyde and nitrotoluene, which are low volatility pollutants. On the basis of previous results, iron chemical catalysis of NO_2 and toluene to generate benzaldehyde is a synergetic process. To analyze the chemical composition of the surface of $\alpha\text{-Fe}_2\text{O}_3$ and BS particles in the presence of toluene and/or NO_2 , high resolution XPS spectra of Fe 2p and Fe 3p were collected. As shown in Figure 4b1, the binding energy decreased with toluene adsorption on BS. The process was proposed to occur via C–H activation of methyl groups followed by hydrogen abstraction via the basic oxygen in the oxide,³⁶ which would result in reduction of the nearby Fe^{3+} to Fe^{2+} (Figure 4). However, the binding energy did not change obviously for the $\alpha\text{-Fe}_2\text{O}_3$ group (Figure 4a1). This phenomenon was similar when UV irradiation was available in the system.

Based on the in situ DRIFTS measurements in different flow systems, two different mechanisms can be proposed for the formation of benzaldehyde and 2-nitrotoluene from the heterogeneous reaction of toluene and NO_2 with iron particles. For benzaldehyde generation, no product was observed when only nitrate was present on $\alpha\text{-Fe}_2\text{O}_3$ and toluene was injected (Figure S11). In this case, the hypothetical reaction between toluene and NO_2 on iron compound surfaces to form benzaldehyde could be as shown in reactions 1–3 below.⁶²

The reaction of toluene and NO_2 to form nitrotoluene on BS is an electrophilic nitration reaction.⁵⁸ This reaction is used in industrial applications to produce mononitrotoluenes, which are recognizable intermediates of many compounds, including pharmaceuticals, dyes, explosives, pesticides, etc.⁶³ It is noted

that the industrial technology for the synthesis of nitroaromatic compounds use mixtures of nitric acids and sulfuric acids. In this study, the BS particle could supply solid acid (sulfate), which provides proton to promote the production of NO_2^+ from nitric acid.⁶⁴ In this reaction, NO_2^+ is considered to be a key reactant in toluene nitration. Based on the DRIFTS results, the peak at approximately 2098 cm^{-1} can be assigned to NO^+ or NO_2^+ .

In summary, benzaldehyde and nitrotoluene could be generated both in the absence and presence of UV irradiation during heterogeneous reactions. The mineral aerosols and NO_2 play important roles during the toluene oxidation and nitration processes. The iron particles could catalyze the oxidation of toluene to form benzaldehyde with NO_2 . Both benzaldehyde and nitrotoluene are recognized as the SOAs during atmosphere process. During smog pollution weather, the contribution of SOAs and secondary inorganic aerosol are found to be of similar importance.⁶⁵ The heterogeneous reactions could be a contributor to SOAs. During the oxidation of toluene with NO_2 , some byproducts (HONO and NO) was formed. Both of the two gases contribute to photochemical smog formation. This phenomenon suggests heterogeneous reactions are important contributors to smog formation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00194.

Characterization of three mineral particles; assignments O 1s XPS results of $\alpha\text{-Fe}_2\text{O}_3$ and BS particles in the absence and presence of UV light; homogeneous reaction results and DRIFTS of three particles to toluene; integrated areas of nitrate, AR, MM, and benzaldehyde at different conditions (PDF)

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Notes

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