

Competing reactions of selected atmospheric gases on Fe₃O₄ nanoparticles surfaces

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Heterogeneous reactions on atmospheric aerosol surfaces are increasingly considered important in understanding aerosol–cloud nucleation and climate change. To understand potential reactions in polluted atmospheres, the co-adsorption of NO₂ and toluene to magnetite (Fe₃O₄ *i.e.* FeO·Fe₂O₃) nanoparticles at ambient conditions was investigated for the first time. The surface area, size distribution, and morphology of Fe₃O₄ nanoparticles were characterized by BET method and high-resolution transmission electron microscopy. Adsorption isotherms, collected by gas chromatography with flame ionization detection, showed that the presence of NO₂ decreased the adsorption of toluene. The analyses of the surface chemical composition of Fe₃O₄ by X-ray photoelectron spectroscopy (XPS) reveal that, upon the addition of NO₂, the surface is oxidized and a contribution at 532.5 ± 0.4 eV in the O 1s spectrum appears, showing that NO₂ likely competes with toluene by dissociating on Fe²⁺ sites and forming NO₃[−]. Different competing effects were observed for oxidized Fe₃O₄; oxidation occurred when exposed solely to NO₂, whereas, the mixture of toluene and NO₂ resulted in a reduction of the surface *i.e.* increased Fe²⁺/Fe³⁺. Analyses by time of flight secondary ion mass spectrometry further suggest toluene reacts with Fe³⁺ sites forming oxygenated organics. Our results indicate that on reduced magnetite, NO₂ is more reactive and competes with toluene; in contrast, on oxidized Fe₃O₄, toluene is more reactive. Because magnetite can assume a range of oxidation ratios in the environment, different competing interactions between pollutants like NO₂ and toluene could influence atmospheric processes, namely, the formation of Fe²⁺ and the formation of atmospheric oxidants.

Introduction

Heterogeneous reactions between trace gases on aerosol particles can strongly affect the chemical and physical properties of the atmosphere.^{1,2}

Iron oxides are important components of aerosol dust particles that can interact with trace gases such as NO₂, H₂O, and organic compounds.^{3,4} The nature of the interaction depends on the properties of the gas and the surface active sites. For example, the first step in the heterogeneous oxidation of NO₂ into NO₃ on α-Fe₂O₃ occurs on the iron site, where NO₂ is reduced to adsorbed NO₂[−](ads).⁵ In contrast, oxidation of SO₂ to SO₄ on α-Fe₂O₃ is suggested to begin on oxygen sites.⁶ In the case of aromatic compounds, the interaction depends on the acid–base properties of the surface.⁷ For instance, α-Fe₂O₃ can dehydrogenate ethylbenzene (EB) due to the weak interaction between hard Fe³⁺ acid sites and the soft basic aromatic ring of EB, whereas, softer Fe²⁺ acidic sites in Fe₃O₄ were inactive due to the stronger adsorption with the soft basic aromatic ring.⁸ Other sites for interaction include surface defects such as oxygen and cation⁹ vacancies. Namely, oxygen vacancies have been proposed to cause a catalytic cycle involving the formation of positive holes, which can oxidize SO₂.¹⁰ The presence of various active sites including iron and oxygen atoms and defect sites give iron oxides adsorptive and redox properties that can alter the physical and chemical properties of the oxide surface and those of the interacting gas.

In atmospheric particles, different types of iron oxides exist and are characterized by crystal structure, which determines other properties such as conductivity and redox behavior.¹¹ Therefore, different phases of iron oxides are likely to display different mechanisms of interaction. For instance, in the presence of NO₂, cation vacancies are suggested to stabilize the formation of nitrosonium in γ-Fe₂O₃, but not on α-Fe₂O₃, where vacancies are absent, resulting in different coordinating environments.⁹ Investigations on the reactivity of iron oxides as components of aerosols have been carried out mainly on α- and γ-Fe₂O₃,^{12,13} and γ-FeOOH phases,¹⁰ which serve as proxies for the iron oxide components in mineral dust, estimated to be the largest contributor to global aerosol mass.¹⁴ In urban and industrial environments; however, aerosol particles originate from industrial¹¹ and traffic emissions,¹⁵ and are composed of different phases of iron oxide: magnetite (Fe₃O₄ *i.e.* FeO·Fe₂O₃) and, its completely oxidized form, maghemite (γ-Fe₂O₃).¹⁵

Magnetite is a mixed valence iron oxide containing Fe²⁺ and Fe³⁺, where the arrangement of Fe²⁺ and half of Fe³⁺ in octahedral sites allows electron hopping giving magnetite near metallic conductivity and unique redox properties.¹⁶ Magnetite has found numerous catalytic applications due to its redox properties.¹⁷ For example at temperatures in the range of 350–600 °C, magnetite catalyzes the dissociation of water and the formation of H₂ gas.¹⁸ In the environment, the adsorptive and redox reactivity of magnetite with contaminants in aqueous and soil systems are known. For example, Fe₃O₄ adsorbs

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metals by electrostatic interactions¹⁹ (e.g., Pb(II),²⁰ Cu(II), Zn(II), Mn(II)¹⁹), and reduces Hg(II) to Hg(0),²¹ nitrobenzene to aniline,²² and Cr(VI) to Cr(III).²³ In the atmosphere, anthropogenic activities involving the burning of fossil fuels emit polluting gases such as polyaromatic hydrocarbons (PAHs),²⁴ BTEX,²⁵ and NO_x²⁶ alongside dust that contains magnetite.¹⁵ A recent field study suggested that the detection of PAHs in dust collected at an industrial area is possibly due to adsorption on magnetite present in the dust.²⁷

Because of rising emissions of anthropogenic dust and gases, particularly in the vicinity of industrial regions,^{28,29} the interaction between Fe₃O₄, as an environmental surface, and polluting gases needs to be investigated. In a previous study, we observed that magnetite nanoparticles adsorbed gaseous benzene, toluene, ethylbenzene, and xylene (BTEX) at ambient conditions;³⁰ the effect of co-pollutants such as NO₂, was not tested, and is the subject of this work. We report the competitive interaction of NO₂ and toluene on Fe₃O₄ nanoparticles (NPs) at room temperature (22 ± 1 °C) and atmospheric pressure (760 ± 5 Torr) using gas chromatography with flame ionization detection (GC-FID) to quantify the adsorption of toluene, and X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion emission mass spectrometry (TOF SIMS) to analyze the chemical composition of the surface. We will discuss the implications of our results on air quality and climate.

Experimental

Synthetic procedure

Fe₃O₄ NPs synthesis. The synthesis of Fe₃O₄ NPs was based on the procedure reported by Vereda *et al.*,³¹ where a 2 : 1 mixture of solid FeCl₃·6H₂O (498%, Sigma Aldrich) and FeCl₂·4H₂O (Z99%, Sigma Aldrich) is dissolved in de-oxygenated water at 85 °C and then co-precipitated by NH₃·H₂O (Z25% NH₃, Fisher Scientific). The NPs were rinsed with de-oxygenated water to remove NH₄Cl by-products.[‡] The rinsed NPs were dried in a vacuum oven at 50 °C and stored in a vacuum desiccator. Water was obtained from a Milli Q (18.2 MΩ cm at 25 °C, Simplicity 185). The initial oxidation ratio of the NPs was controlled by the number of washings with water, *i.e.*, the higher the number of washings, the more oxidized the Fe₃O₄ NPs. To characterize potential maghemite formation, X-ray diffraction (XRD) patterns show the bulk of nanoparticles was made of magnetite. With respect to XPS spectral fitting, applying constraints that correspond to maghemite alone and other phases of iron oxides (e.g., FeO), did not reproduce the experimental data. Moreover, the solid synthesized powder was black, which points to magnetite. Note that considering that the NPs are 5–20 nm in size with an average size of 9 nm and that the escape depth of XPS is in that same order of a few nm (1–10 nm),³² the spectra obtained are reflective of the whole particle and not just the surface. On that basis and considering that the experiments were carried out in dry air and at room temperature, any oxidation is expected to be related to Fe²⁺ from magnetite resulting in maghemite, the most favorable oxidation product. In addition, the uptake of Fe(II) as a sorbed species to magnetite in aqueous media has been shown to be unlikely and that a partially oxidized magnetite phase was more likely to form.²²

Characterization methods

The Fe₃O₄ NPs were characterized using several techniques. The crystal structure and the average Scherrer size were determined from X-ray diffraction (XRD) patterns. Details on the collection of XRD patterns are given in Table S1 (ESI†). The morphology and size distribution of the Fe₃O₄ NPs were determined from images collected by means of transmission electron microscopy (Philips CM200 TEM). The Brunauer–Emmett–Teller (BET) specific surface area (SSA) and the Barrett–Joyner–Halenda (BJH) average pore size were determined using a surface area analyzer at –196 °C (TriStar 3000 V6.07 A). The TEM, SSA, and BJH pore size results are representative of a typical batch of Fe₃O₄ NPs prepared by co-precipitation of iron salts.

Adsorption and surface analyses by XPS and TOF SIMS experiments

Adsorption isotherm reactions. The adsorption experiments were reproduced several times on different batches of NPs; here, we present one set of adsorption isotherms from a typical adsorption reaction carried out on two fractions from a batch labeled S_{adsorption}. One of the principal objectives of this study was to investigate the system at conditions relevant to the environment. To this end, solid-phase micro-extraction (SPME) by means of a Carboxen/poly(dimethylsiloxane) (CAR/PDMS) fibre (Sigma Aldrich) was used to pre-concentrate and detect low ppmv levels of toluene. The CAR/PDMS SPME fibre consists of a fused silica fibre coated with PDMS in which porous carbon particles are embedded rendering it suitable for the sampling of volatile organic compounds.³³ Using SPME, the lower range concentrations were well reproduced. At higher concentrations of analyte, however, SPME is not well

adapted³⁴ and large uncertainties result. Therefore, the majority of the isotherm data points were collected in the low concentration range of toluene.

Surface analyses by XPS and TOF SIMS. For the analyses by XPS, three fractions from each of two batches of Fe₃O₄ NPs, S_{reduced} and S_{oxidized}, were subjected to different experimental conditions. For the analyses by TOF SIMS, four additional fractions from the S_{oxidized} were tested. All experiments were carried out at room temperature (22 ± 1 °C) and atmospheric pressure (760 ± 5 Torr). As the NPs were in powdered form and magnetic, after weighing, a magnetic stirring bar coated with Teflon was used to collect the powder. Both the magnetic bar and the powder were transferred to glass flasks, sealed with Teflon caps and stoppers. The adsorption isotherms were collected over a period of 7–8 hours. We had previously observed that the adsorption occurred on a time scale of several minutes and determined the time for diffusion of toluene as 15 minutes. The duration between two points of the isotherm is approximately 40 minutes, since several experimental conditions were tested simultaneously in different flasks to assure data quality. As such, we performed control tests containing toluene only and serving to construct the calibration curve, the reference and the targeted experiment. With respect to TOF SIMS and XPS experiments, the NPs were exposed to the respective gas mixtures for ca. 18 hours prior to analysis.

All the flasks were Pyrex glass, pre-coated with a hydrophobic layer of Glassclad 18 (United Chemical Technologies³⁵). Prior to adsorption experiments, the flasks were washed using hydrochloric acid, followed by rinsing with water; subsequently with glassware soap and then with at least two portions of 20 mL of acetone. The glass flasks were placed in an air ventilated oven at 120 °C for a minimum of 12 hours. All openings were sealed with Teflon stoppers, which were also rinsed with soapy water and dried by pure airflow. To ensure the absence of organic residues, the preparation of each flask prior to the experiment started with the evacuation to at least 2×10^{-2} Torr for 20 minutes using a Schlenk vacuum system. Then the flasks were filled with UHP N₂ to 760 ± 5 Torr and re-evacuated to low 10^{-2} – 10^{-3} Torr. This cycle was repeated once more, and after the second evacuation, the flask was filled by extra dry air (O₂ 19.5–23.5% and H₂O < 10 ppm, Praxair Canada, Inc.) to 760 ± 5 Torr. The flasks were then placed on stirring plates and allowed to stir for at least 15 minutes and then sampled and analyzed using SPME and GC-FID (HP 6890)

equipped with a general purpose column (HP5 MS, Agilent). A peak assigned to toluene was sometimes detected, in which case the flask was subjected to further cleaning. The flasks were also analyzed by GC-MS (HP 5973, Agilent) and an HP5 MS column in scan mode verified that organic residues were not present. The chromatogram of a typical flask prior to the addition of toluene and NO₂ is shown in Fig. S1 in the ESI.† Therefore, it is not likely that organic residues were left on the walls of the flasks in quantities sufficient to impact the reaction.

Preparation of gas mixtures. For the mixture of toluene (99.8%, Fisher Scientific), liquid toluene was injected into the flask and two pump–freeze–thaw purification cycles were carried out. After the second thaw, the pressure of toluene was measured at room temperature (22 ± 1 °C). NO₂ was directly transferred from a premixed 1.02% NO₂ in N₂ (Praxair Canada, Inc.) mixture into another flask. Ultrahigh purity (UHP) N₂ (99.999%, MEGS Specialty Gases) was used to complete toluene and NO₂ mixtures to 760 ± 5 Torr. Toluene and/or NO₂ were injected in the reaction flasks with gas tight syringes (Hamilton Company Inc.).

Adsorption reactions. By injecting increments of toluene into three reaction flasks, a control, a reference, and a test, adsorption isotherms of toluene on Fe₃O₄ NPs, in the presence and absence of NO₂, were collected. Prior to toluene and NO₂ injections, the flasks containing the Fe₃O₄ NPs were evacuated for 20 minutes (down to 6×10^{-2} Torr), flushed with UHP N₂, and then filled with extra dry air. Experimental conditions are summarized in Table 1.

The amount of toluene adsorbed was determined using a CAR/PDMS SPME fibre for sampling and a GC-FID (HP 6890) for quantification. Details on data acquisition are given in the ESI.†

A calibration curve relating the FID's response (peak areas) to the range of concentrations tested was constructed using the control flask, and was used to determine the amount of toluene at equilibrium in the reference or test flasks. The amount of adsorbed toluene was calculated by subtracting the amount at equilibrium (in the reference or test flasks) from that in the control. We plotted the amount of toluene adsorbed per gram of Fe₃O₄ NPs as a function of the concentration of toluene remaining in the gas phase, and used adsorption models to reproduce the data. Origin Pro.8 software was used for linear and nonlinear regression of the calibration curve and adsorption isotherms, respectively.

Surface analyses with XPS and TOF SIMS. Identical preparation procedures as those for adsorption reactions were followed for each fraction of each batch with the exception of the concentration tested and the weight of NPs used. Table 1 shows the experimental conditions. High resolution XPS scans of the carbon C1s, oxygen O1s, iron Fe2p, and N1s core lines of Fe₃O₄ NPs were collected by means of an XPS unit (ESCALAB 3 MKII de VG) with a non-monochromatic Al K α source

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operated at pass energy of 20 eV and step size of 0.05 eV at a resolution of 0.85 eV. All binding energies reported in this work are within 0.4 eV. The spectral analyses of the scans were carried out using the Advantage software³⁶ (Thermo Scientific). Details on the spectral fitting, peak assignments for Fe2p, and C1s spectra are presented in Fig. S2 and S3 and Table S2 (ESI†). TOF SIMS mass to charge spectra of Fe₃O₄ NPs were obtained for positive and negative ions on a unit (ION-TOFSIMS IV) with a Bi⁺ ion source at 25 kV.

Table 1 Experimental conditions for adsorption and surface analyses

	Toluene (ppmv)	NO ₂ (ppmv)	Fe ₃ O ₄ NPs (g) \pm 2.0×10^{-4}
Adsorption			S _{adsorption}
Control	0–1200	1.5	—
Reference	0–1200		0.14
Test	0–1200	1.5	0.14
XPS			S _{reduced}
(a)	—	—	0.02
(b)	13	—	0.02
(c)	13	0.65	0.02
XPS and TOF SIMS			S _{oxidized}
(a)	—	—	0.02
(b)	13	—	0.02
(c)	13	0.65	0.02

Results and discussion

Characterization of the Fe₃O₄ NPs

The XRD patterns of Fe₃O₄ NPs in Fig. 1 show that relative intensity peaks for S_{adsorption}, S_{reduced}, and S_{oxidized} matched those of the reference Fe₃O₄, for which the Scherrer size was calculated as 8 and 9 nm,³⁷ respectively.

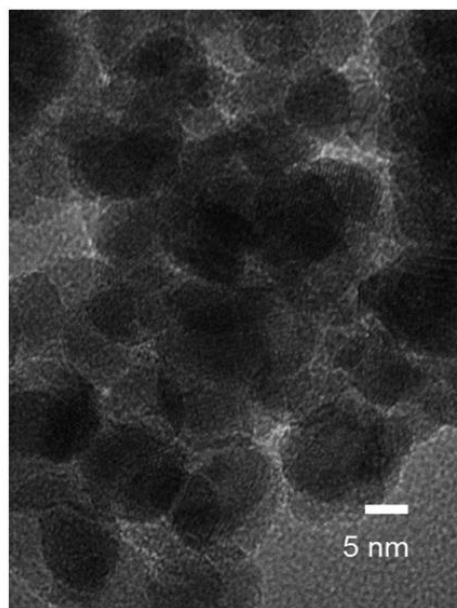


Fig. 2 A typical high resolution TEM image depicting the size distribution and crystallinity of Fe₃O₄ NPs prepared by co-precipitation.

For a typical Fe₃O₄ prepared by co-precipitation, the SSA was 80 10 m² g⁻¹ and the average pore width was 10 3 nm varying from 5–50 nm,³⁰ which indicates NPs were mesoporous.³⁸ The TEM image in Fig. 2 shows the size distribution of the Fe₃O₄ NPs was in the range of 5–10 nm and the NPs were crystalline. The size range and pore widths of the NPs indicate they were geometrically heterogeneous.

Adsorption reactions

Competitive adsorption of toluene and NO₂ on Fe₃O₄ NPs. To investigate the effects of NO₂ on the adsorption of toluene on Fe₃O₄ NPs, adsorption isotherms of toluene, alone and in the presence of 1.5 parts-per-million by volume (ppmv) NO₂, were collected. The adsorption experiments were carried out several times and the trend of a decrease in the adsorption of toluene in the presence of NO₂ is reproduced for seven independent experiments, but to different extents. The variability in the adsorption capacity of toluene to the NPs was observed and ranged from 10 to 40% across different batches of NPs. A batch corresponds to a single separate synthesis of NPs.

This variability is attributed to the variability existing across different batches of the NPs. The variability between batches of NPs is likely related to different initial oxidation levels of the different batches used and the size distribution and morphology. The latter would affect the surface area available, while the former would influence specific sites for adsorption (Fe²⁺ and Fe³⁺) and properties such as acid–base character. The oxidation level of a batch of NPs could have been affected by the time required for drying and the storage time from synthesis to use. The highest vacuum during drying and storage was 18 Torr, which means that the NPs could have been exposed to air. Magnetite is sensitive to oxygen in air and a layer of oxidized magnetite (*i.e.* maghemite γ-Fe₂O₃) is known to form on the surface,³⁹ resulting in different initial oxidation levels. With respect to the variability in size and morphology, the synthesis of NPs by co-precipitation results in polydispersed samples due to the mechanism of formation (during nucleation and growth stages).⁴⁰ Inhomogeneity of the sizes of the NPs could affect the available sites for adsorption and result in the variability with respect to the extent of adsorption. Prior to adsorption and characterization experiments, the NPs were crushed with a mortar and pestle, which results in variability in size as observed in the TEM image (Fig. 2). For each set of experiments comprised of toluene and toluene + NO₂, fractions of NPs came from the same batch. Examples of other adsorption experiments are given in the ESI† (Fig. S4 and S5). A typical adsorption

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experiment is shown in Fig. 3, where the adsorption of toluene on Fe₃O₄ NPs is reduced in the presence of NO₂. The reduction in the adsorption of toluene on a related oxide, Fe₂O₃ in the presence of NO₂ has been observed (at 117 °C).⁴¹ The reduction in the amount of toluene adsorbed indicates that NO₂ competes with toluene in the same sites.

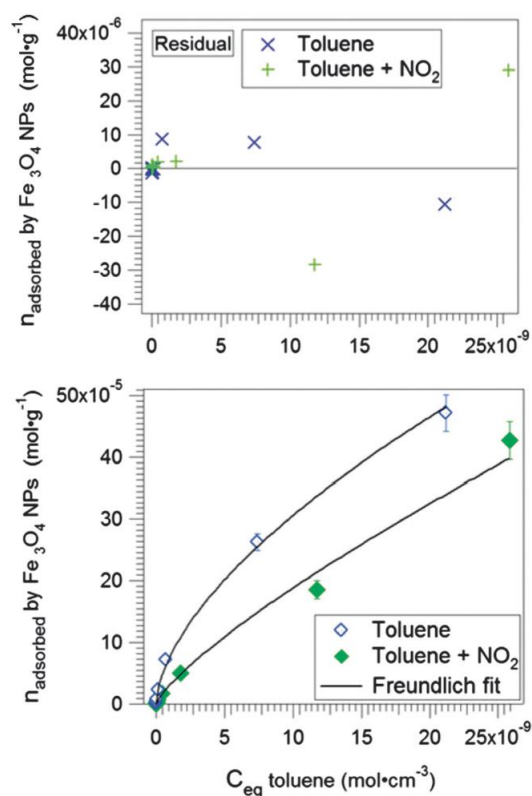


Fig. 3 Experimental and fitted adsorption isotherms (bottom graph) and residual of the fit (top graph) of toluene on Fe₃O₄ NPs in dry air alone (blue empty diamonds) and in the presence of NO₂ (green filled diamonds). Error bars represent standard errors calculated by the propagation of errors during preparation and analyses. The limit of detection of toluene is $(3.3 \times 10^{-13}) \pm (3.1 \times 10^{-25})$ mol cm⁻³. 1 ppmv of toluene = 4.11×10^{-11} mol cm⁻³.

To further examine the mechanism by which NO₂ reduces the adsorption of toluene, several adsorption models frequently used to represent vapor–solid adsorption were attempted including Langmuir,⁴² Freundlich,⁴³ Toth,⁴⁴ Sips,⁴⁵ Redlich–Peterson,⁴⁶ and dissociative Langmuir.⁴⁷ These models differ in the assumptions made to describe the adsorption of vapor to a surface. Table S3 (ESI†) enlists the models used, their respective assumptions and parameters (e.g., energy of sites, interactions between adsorbed molecules *etc.*). The parameters relevant to each model were determined by nonlinear regression method based on the minimization of w^2 . The resulting fits and residuals for the models tested are plotted in Fig. S6 (ESI†) and the respective values for the parameters are presented in Table S4 in the ESI.† Among the tested models, RP, Toth, Sips, and Freundlich appear to reproduce the observed isotherm more adequately at the higher concentration. In both Toth and Sips test models, however, the fitting resulted in higher standard errors on the measured parameters.

To evaluate the RP and Freundlich test models, we used the comparison fitting tool in OriginPro 8⁵⁴⁸ based on the AIC criterion test, which ranks the models in order of most justified to represent the data and has been used in several previous adsorption/ desorption modeling studies.^{49,50} Details on the calculations are presented in the ESI.† On the basis of the AIC criterion, the RP model is 0.38 times more likely to be correct. In other words, both Freundlich and RP are similar. Since the number of data points modeled was 10, we selected the model with fewer parameters (*i.e.*, Freundlich). The Freundlich model is represented by eqn (1):

$$n_{ads} = K_F C_{eq}^{\frac{1}{n}} \quad (1)$$

where the constants K_F and n represent the Freundlich constants. The residuals are shown in the top graph in Fig. 3.

The parameter values for the Freundlich model are shown in Table 2. The Freundlich model describes adsorption on energetically heterogeneous sites.⁵¹ The constants, K_F and n , are specific to the adsorption system and depend on temperature. Together, K_F and n provide a measure of adsorption capacity that depends on the heterogeneity⁵² in the system due to lateral interaction and surface sites (geometric and chemical), which are encompassed in ' n '.⁵³ Therefore, the use of the Freundlich model suggests that the adsorption mechanism of toluene occurs on heterogeneous sites, which could be explained by the range of sizes and pore widths of NPs (Fig. 2), but also by the presence of Fe^{2+} and Fe^{3+} as chemically heterogeneous sites. The Freundlich isotherm has been reported to model toluene vapor on heterogeneous surfaces like soil,⁵⁴ and carbon nanotubes,⁵⁵ and the adsorption of heavy metals from aqueous media on Fe_3O_4 ,²⁰ and on $\gamma\text{-}Fe_2O_3$.⁵⁶

In the presence of NO_2 , despite showing the best fit for the data, a large standard error in the K_F value suggests the model may be oversimplifying the interaction of toluene. Nevertheless, if we compare the ' n ' values, the system involving NO_2 has a lower value. Because ' n ' is sensitive to the composition of the adsorption system,⁵² a lower ' n ' implies that NO_2 influences the adsorption of toluene by decreasing heterogeneous processes. There are several processes that can be affected by NO_2 such as blocking sites (e.g., pores), and/or reacting with the active sites for adsorption of toluene (i.e. Fe^{2+} and Fe^{3+}). To further understand the mechanism by which NO_2 competes with toluene, surface analyses of the Fe_3O_4 were carried out by XPS and TOF SIMS and are discussed in the next section.

Table 2 Parameter values for the Freundlich fit of the adsorption isotherms of toluene on Fe_3O_4 NPs in dry air alone and in the presence of NO_2

Parameters	Toluene	Toluene + NO_2
K_F ($cm^{-3} g^{-1}$)	$(2.01 \times 10^1) \pm 4.6$	$(3.75 \pm 2.24) \times 10^2$
n	$1.66 \pm (3.2 \times 10^{-2})$	$1.27 \pm (5.1 \times 10^{-2})$

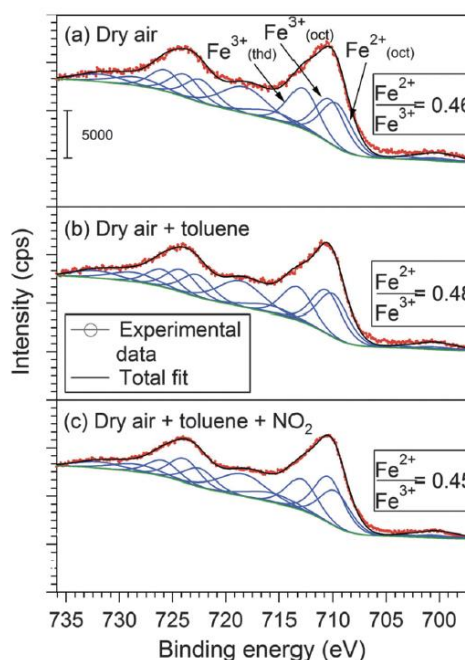


Fig. 5 Fe2p XPS fitted spectra for fractions from $S_{reduced}$.

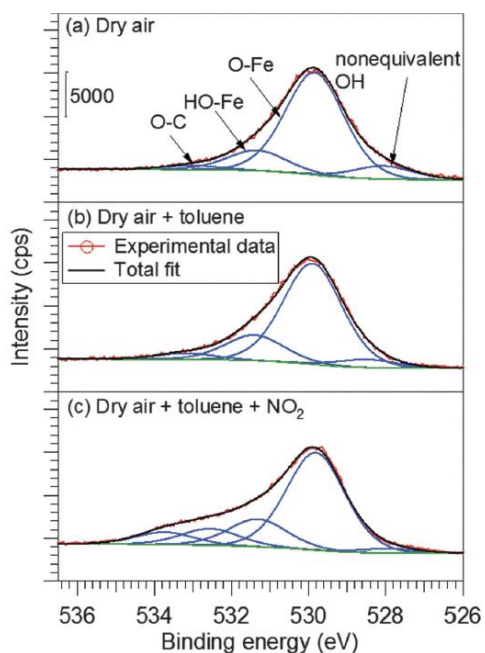


Fig. 4 O1s XPS fitted spectra for fractions from S_{reduced} .

XPS and TOF SIMS of samples exposed to dry air only. To analyze the chemical composition of the surface of Fe₃O₄ NPs in dry air and in the presence of toluene and/or NO₂, the high resolution spectra XPS of O1s and Fe2p were collected. The XPS O1s and Fe2p spectra in dry air only are shown in Fig. 4(a) and 5(a), for the fraction from batch S_{reduced}, and Fig. 6(a) and 7(a), for the fraction from S_{oxidized}. The O1s spectra in Fig. 4(a) and 6(a) are fitted with 3 peaks at 529.8 eV, 531.3 eV, and 533.0 eV, which were assigned to the main oxide FeO, lattice FeOH and/or adsorbed hydroxyl, and (O–C) and/or adsorbed water, respectively. The peak at 533.0 eV can be assigned to water, but also to organic O(O–C).^{57,58} The atomic percent contribution of the O–C in the O1s correlates with that in the C1s (S2 and S3, ESI†). Therefore, the peak is likely O–C. Since adsorbed water can also be found due to moisture in the air, it cannot be ruled out as another potential adsorbed species. The source of the carbon contamination is due to air exposure and possibly reactions involving CO₂ at vacuum levels during the XPS analysis.⁵⁹ With respect to adsorbed moisture, studies on hydrated iron films show that carbon contamination may also dissolve into the water layer and result in the contribution for O–C.⁶⁰ These values are consistent with reported values for Fe₃O₄, as shown in Table 3. A contribution at 528 eV was added, and is likely a hydroxyl group. Peaks below the main oxide have been assigned to chemisorbed oxygen and hydroxyl groups at non-equivalent sites of Fe₃O₄ exposed to H₂O.⁶¹ Note that the formation of strongly bound hydroxyl groups⁶² on magnetite occurs due to the dissociation of moisture, which is reported for H₂O present at pressures as low as 10^{–4} Torr,⁶¹ and could form during sample preparation (e.g., weighing and transferring). The Fe2p spectra in Fig. 5(a) and 7(a) show the Fe²⁺/Fe³⁺ were 0.46 and 0.38 for S_{reduced} and S_{oxidized}, respectively. Note that stoichiometric Fe₃O₄ has a ratio of 0.50. The estimated random error on all reported Fe²⁺/Fe³⁺ ratio values are presented in Table 3; details are given in the ESI.†

Interaction of toluene with Fe₃O₄ NPs. Using XPS, the primary objective was to examine changes in the surface redox ratio. In the presence of toluene, Fig. 5(a) and (b) show that Fe²⁺/Fe³⁺ increases slightly from 0.46 to 0.48, but is within experimental uncertainty. In the case of S_{oxidized} exposed to 13 ppmv of toluene, contamination on the carbon spectrum was observed and the sample was excluded from the comparison. However, during the same set of experiments, a fraction of S_{oxidized} exposed to 100 ppmv of toluene (in dry air) was tested and the Fe²⁺/Fe³⁺ increased from 0.38 to 0.49, shown in Fig. 7(a) and (b) and Table 3. We had previously observed an increase in the Fe²⁺/Fe³⁺ when exposed to toluene.³⁰ The increase in the Fe²⁺/Fe³⁺ ratio could result if toluene reacts on the Fe₃O₄. More details on the uncertainties associated with the changes in the Fe²⁺/Fe³⁺ in the presence of toluene alone are given in the ESI.†

With respect to the XPS O1s spectra, an increase in the ratio

of organic oxygen/total O is observed for both S_{reduced} and S_{oxidized} samples exposed to toluene alone, as shown in Table 3. The contributions assigned to organic oxygen are consistent with organic carbon observed in the C1s. In the case of S_{reduced}, there is a decrease in the Fe/O when toluene is added, which appears to be consistent with the increase in the organic oxygen. Note that the initial Fe/O is larger than the theoretical value of 0.75. The reason for the higher content of iron is unclear. In the case of S_{oxidized}, the Fe/O is constant and is inconsistent with the increase in the organic O. However, the ratio of organic oxygen/Fe–O (oxide) increases for both S_{reduced} and S_{oxidized} when exposed to toluene. The increase in the organic oxygen appears to occur at the expense of the oxide suggesting that toluene interacts with the oxygen from the oxide; yet it is noteworthy that these changes are close to the uncertainty limits, a definite mechanism cannot thus be confirmed at this stage. In Table 4, the TOF SIMS analyses for fractions exposed to toluene show increases in the normalized intensities for fragments associated with toluene at *m/z* of 77 and 91. The increase in fragments at *m/z* 43 and 105, associated with oxygenated compounds further hint that toluene is reacting. The TOF SIMS spectra showing the total intensity of the fragments having *m/z* of 43, 77, 91, and 105 for the fractions of Fe₃O₄ NP exposed to various conditions (Table 1) are shown in Fig. S7–S10 in the ESI.† Note that the inherent presence of hydrocarbons as impurities in TOF SIMS analyses precludes a definite reactive mechanism which is to be ascertained. Under conditions similar to those used here, the adsorption of toluene on Fe₃O₄ is explained by the acid–base properties of the system, where the aromatic ring (base site) interacts with the partially filled d-shells of the iron cations (acid site), an interaction observed for other oxides⁷ and, between cations and polyaromatic compounds in soils⁶³ (and references therein).

Reactions of aromatic compounds adsorbed on metal oxides

have been observed under non-ambient conditions e.g., at temperatures greater than 300 °C.⁶⁴ For example, the dehydrogenation of ethylbenzene (EB) on α-Fe₂O₃, and the oxidation of toluene on iron based catalysts⁶⁴ were proposed to occur via C–H activation of the ethyl and methyl groups followed by hydrogen abstraction by basic oxygen in the oxide, which in the case of EB was proposed to cause a reduction of the nearby Fe³⁺ to Fe²⁺.^{8,65}

Since all experiments were performed at room temperature, it is proposed that the reactivity be associated with

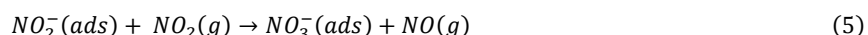
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defects and/or nanoscale effects of Fe₃O₄ NPs. Step defects on α-Fe₂O₃ have been proposed to cause adsorption of EB in a particular configuration favoring H-abstraction.⁶⁶ Defects such as oxygen vacancies, known to occur in solids to maintain charge neutrality,⁶⁷ are another type of reactive sites reported for iron oxides; the adsorption of oxygen in those vacancies results in reactive oxygen species.⁶⁸ In an iron supported catalyst, vacancies influenced the configuration of the adsorbing oxygen into an angular arrangement that enhanced CO oxidation.⁶⁸ Here, Fe₃O₄ NPs samples were exposed to oxygen (*ca.*, 760 Torr of dry air) prior to toluene addition, therefore, the presence of oxygen vacancies as direct active sites is unlikely as oxygen would adsorb onto them; the presence of reactive oxygen species, however, cannot be precluded.

In addition, nanoscale effects can influence reactivity due to enhanced acid–base properties.⁶⁹ On a related oxide, higher basicity of surface oxygen atoms for smaller α-Fe₂O₃ NPs were proposed to explain increased oxidation of Mn²⁺.⁷⁰ Alternatively, the adsorption of toluene could induce charge rearrangement. The effect of water adsorbed on the surface arrangement of iron cations in magnetite has been proposed in a recent theoretical study.⁷¹ In summary, these results point to a complex interaction of toluene on Fe₃O₄ NPs, where the observed increases in the Fe²⁺/Fe³⁺ ratio and in the contributions assigned to organic oxygen could be due to the oxidation of toluene by surface oxygen on Fe₃O₄ NPs and the possible formation of an oxygenated organic.

Oxidation of Fe₃O₄ NPs by NO₂. For the mixture of toluene and NO₂, the Fe²⁺/Fe³⁺ values of S_{reduced} are lower but within the error when compared with the fraction exposed to toluene shown in Fig. 5(b) and (c). By comparing the Fe/O ratios, a decrease is observed, as shown in Table 3, and is consistent with the addition of oxygen, which supports the oxidation of the surface. In contrast, the fraction from S_{oxidized} in Fig. 7(c) has a higher Fe²⁺/Fe³⁺ compared with the sample in air (Fig. 7(a)), while the Fe/O remains constant suggesting that a different mode of interaction is occurring and preventing NO₂ from oxidizing the surface. Note that the effect of NO₂ alone on the Fe₃O₄ NPs was beyond the scope of the study; however, a fraction of S_{oxidized} exposed to NO₂ only, results in the highest decrease in the Fe²⁺/Fe³⁺ ratio, *i.e.* in the oxidation of Fe₃O₄ NPs and is shown in Table S5 in the ESI.† In summary, the results show that the addition of NO₂ causes an oxidation of the surface, but that its competing effects on the adsorption of toluene depend on the initial stoichiometric ratio of magnetite. For consistency, S_{oxidized} exposed to 100 ppmv of toluene was not used for comparison since the other samples were exposed to only 13 ppmv (see previous section).

In the atmosphere, the reactions of NO₂ and hydrocarbons are influenced by the presence of hydroxyl radicals, which are formed photochemically at wavelengths in the UV (O₃ < 319 nm, O₃ formation from NO₂ < 424 nm).⁷² In our experiments, however, radiation was not applied and hydroxyl radicals in the gas phase were not present. Further qualitative and quantitative analyses by GC-MS showing that NO₂ and toluene did not react in the gas phase are given in Fig. S1 in the ESI.† Therefore, the changes observed are attributed to surface reactions on the Fe₃O₄ NPs. The interaction of NO₂ with metals has been proposed to occur by adsorbing to the metal site⁷³ and partially dissociating into NO₃[−] and NO *via* the formation of NO₂[−],⁹ following equation (2)–(4) or (5):



The oxidation of magnetite is proposed to be due to the reduction of NO₂ to NO₂[−] on the iron sites *i.e.* the same active sites for toluene.

Table 3 Assignments of binding energies (in eV) and ratios calculated from high resolution fitted spectra of Fe2p and O1s XPS for fractions of Fe₃O₄ NPs exposed to different experimental conditions

Assigned species, reported literature BE	S _{reduced}			S _{oxidized}		
	Dry air	Toluene	NO ₂ + toluene	Dry air	Toluene ^a	NO ₂ + toluene
OH (nonequivalent): −1.6, O ^{2−} (undercoordinated): −1 (rel. Fe–O) ⁶¹	528.1	528.5	527.9	527.4	527.3	528.1
O–Fe: 529.9 ± 0.4, ⁸² 530.1 ± 0.2 ⁸³	529.8	529.9	529.8	529.8	529.9	529.9
HO–Fe, adsorbed O, O=C: 531.4 ± 0.2, ⁸³ 531.6, ³⁹ 531.3, 531.9–532.8 ⁸⁸	531.3	531.4	531.3	531.3	531.3	531.4
NO ₂ /NO ₃ (on TiO ₂): 532.5/533 ⁷⁴			532.6			
O–C: 532.4–533.5 ⁵⁸						
H ₂ O on Fe ₃ O ₄ : 532.7 ± 0.1 γ-Fe ₂ O ₃ : 533.3 ± 0.1 ⁵⁷	533.0	533.2		533.0	533.0	533.3
H ₂ O (molecular): 534 ⁶¹			533.7			
Fe ²⁺ /Fe ³⁺	0.46 ± 2.6 × 10 ^{−2}	0.48 ± 2.8 × 10 ^{−2}	0.45 ± 2.8 × 10 ^{−2}	0.38 ± 2.0 × 10 ^{−2}	0.49 ± 2.7 × 10 ^{−2}	0.43 ± 2.9 × 10 ^{−2}
Fe/O	0.80 ± 2.7 × 10 ^{−2}	0.74 ± 2.5 × 10 ^{−2}	0.63 ± 1.9 × 10 ^{−2}	0.70 ± 2.4 × 10 ^{−2}	0.70 ± 2.3 × 10 ^{−2}	0.71 ± 2.9 × 10 ^{−2}
O > 531.2 eV/O (total)	0.030 ± 4.1 × 10 ^{−3}	0.040 ± 5.1 × 10 ^{−3}	0.19 ± 9.9 × 10 ^{−3}	0.053 ± 5.2 × 10 ^{−3}	0.065 ± 5.6 × 10 ^{−3}	0.059 ± 6.6 × 10 ^{−3}
O > 531.2 eV/Fe–O (non equiv., FeOH and FeO)	0.030 ± 4.3 × 10 ^{−3}	0.046 ± 5.3 × 10 ^{−3}	0.23 ± 1.3 × 10 ^{−2}	0.056 ± 5.5 × 10 ^{−3}	0.069 ± 6.0 × 10 ^{−3}	0.063 ± 7.1 × 10 ^{−3}
FeOH (including peak at 528)/FeO	0.33 ± 1.4 × 10 ^{−3}	0.33 ± 1.2 × 10 ^{−2}	0.31 ± 1.0 × 10 ^{−2}	0.24 ± 1.4 × 10 ^{−2}	0.23 ± 1.3 × 10 ^{−2}	0.27 ± 1.8 × 10 ^{−2}

^a Toluene concentration 100 ppmv.

In addition to oxidation, changes in the oxygen O1s of S_{reduced} when NO_2 is added (Fig. 4(c)) are observed. An increase in oxygen is observed for the organic O/O (total) ratio compared with the fraction exposed to air or toluene alone, as shown in Fig. 4(a)–(c) and Table 3 for S_{reduced} . A peak at 532.6 eV has only been observed on the S_{reduced} sample. Peaks at binding energies in the range of 532.5–534 eV are assigned to organic oxygen and adsorbed water, but could also be attributed to NO_3 and/or NO_2 at 532.5 eV and 533 eV, respectively.⁷⁴ However, the N1s spectra did not show peaks in the NO_2/NO_3 region and the TOF SIMS spectra did not positively confirm m/z of 46 (NO_2^-) or 62 (NO_3^-), which is explained by the low concentrations of NO_2 used in this work (0.65 ppmv). Nevertheless, a mechanism involving the formation of NO_3 cannot be ruled out. By comparing with the C1s (Fig. S2, ESI†), a peak at 289 eV consistent with organic oxygen is observed. At this stage, however, we cannot confirm the identity of the peak at 532.5 eV, which appears to be related to the addition of NO_2 . In the case of S_{oxidized} ratios involving oxygen species are within uncertainty range, as depicted in Fig. 6(c) and Table 3. An increase in the organic O/O (total) is also observed for S_{oxidized} exposed to NO_2 alone, as shown in Table S5 in the ESI.†

Because the surface contains hydroxy groups, an additional pathway relevant for the reaction of NO_2 on hydroxylated surface involves the formation of nitrate and H_2O , which has been reported on metal oxide.⁷⁵ Alternatively, it has also been observed that the strong interaction of NO_2 with the metal center on the hydroxylated surface of molybdenum oxide caused the displacement of OH and its recombination into H_2O rather than reacting and forming of HNO_3 ,⁷⁶ as is typically reported for metal oxides. It cannot be ruled out that water forms and as previously mentioned carbon contaminants may dissolve giving rise to the organic carbon contributions.

To summarize, fractions from the S_{reduced} , which contained OH groups at low BE and had a higher initial $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, were more reactive towards NO_2 compared with the fractions from the S_{oxidized} batch, where OH was absent and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was lower. The binding environment of OH has been shown to influence the reactivity of related iron oxyhydroxides FeOOH .⁷⁷ Here, the exact coordinated environments of oxygen atoms on Fe_3O_4 cannot be extracted by XPS due to overlapping binding energies; further studies on the coordinating environment of OH on magnetite, and the respective interactions with NO_2 are needed to understand the associated reactivity.

These results show that the mixture of toluene and NO_2 interacts on the reduced and oxidized samples *via* different pathways. In the case of reduced magnetite, the observed oxidation (decrease in $\text{Fe}^{2+}/\text{Fe}^{3+}$ and increase in oxygen) and the peak at 532.5 eV suggest that NO_2 either competes with toluene or is involved in the oxidation of toluene. In contrast, on the oxidized sample, the mixture of toluene and NO_2 results in an increase in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio pointing to a different reaction mechanism, where toluene either competes with NO_2 and/or reverses oxidation by interacting with the iron sites.

The difference in the initial stoichiometric ratio suggests that NO_2 is more reactive on reduced Fe_3O_4 . On g- Fe_2O_3 studies have shown that the reaction of NO_2 forming NO_3 likely involves two NO_2^- adsorbed (eqn (4)),⁹ and depends on the concentration of adsorbed NO_2^- . Therefore, the presence of more Fe^{2+} could result in the formation of more adsorbed NO_2^- , and possibly NO_3^- on the reduced sample. The higher reactivity of reduced Fe_3O_4 compared with its more oxidized counterpart has been reported for other systems.^{78,79} For instance, in the reduction of Cr^{+6} , where Fe^{2+} donate electrons to drive the reaction, the formation of an oxidized layer of g- Fe_2O_3 inhibited further reaction,⁸⁰ in aqueous media. The results indicate that the stoichiometry of magnetite will determine the competing effects in a reaction mixture of toluene and NO_2 , where reduced surfaces will get oxidized and form an irreversible product, while oxidized surfaces would be less reactive towards NO_2 allowing toluene to interact and result in an increase of Fe^{2+} .

At this stage, we cannot propose a definitive mechanism(s) on how toluene competes with NO_2 for adsorption onto oxidized samples of Fe_3O_4 NPs; yet it is logical to speculate that either toluene occupies Fe^{2+} sites or it can displace NO_2 before the formation of NO_2^- . The formation of NO_2^- has been reported as the rate limiting step in the production of NO_3 on g- Fe_2O_3 ,⁹ hence could be hindered by less availability of Fe^{2+} , which results in less conductivity and electron flow necessary for the formation of NO_2^- . The reactivity of NO_2 is influenced by the nature of the active sites, which differ for iron oxides polymorphs. Namely, in addition to iron sites, cation vacancies on g- Fe_2O_3 have been linked to reactive sites that cause various coordination environments in comparison with a- Fe_2O_3 .⁹ Here, oxidized magnetite contains g- Fe_2O_3 , which may allow a different formation reaction pathway in comparison with reduced Fe_3O_4 . With respect to oxygen vacancies, known to form reactive oxygen by adsorbing oxygen,⁸¹ and to influence the interaction of NO_2 with other metal oxides,⁷³ as with toluene, it is unlikely that they are present as direct active sites for NO_2 in dry air. The presence of adsorbed reactive oxygen, however, cannot be ruled out. Reactive oxygen species have been proposed to cause an increase in positive holes that can adsorb and oxidize SO_2 to SO_4 on a- Fe_2O_3 ,¹⁰ and to adsorb in a particular configuration that allowed subsequent reaction with CO forming CO_2 on an a- Fe_2O_3 based catalyst.⁶⁸

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Here, our results suggest that NO₂ interacts with iron sites, yet it is possible that if reactive oxygen species are present, the coordinating environment of NO₂ on iron sites be affected influencing the formation of nitrate.⁸¹ Future investigations should include studying the reaction intermediates on Fe₃O₄ samples of varying stoichiometric ratios. Future vibrational spectroscopy studies might be helpful to ascertain reactive species on the surfaces.

Conclusion

In this work, we studied for the first time the interaction of NO₂ and toluene on Fe₃O₄ NPs, to investigate potential reactions on industrial dust aerosols. The reduction in the adsorption of toluene when NO₂ is added indicates a competition for active sites.

The competing effect of NO₂ was explained by its reactivity with magnetite, which is suggested to depend on the availability of Fe²⁺ and possibly OH⁻. Previous studies in aqueous systems have established the importance of Fe²⁺ (ref. 84) in the reactivity of magnetite.⁸⁵ The results presented here expand on the importance of Fe²⁺ and stoichiometry of Fe₃O₄, as well as the possible influence of reactive oxygen species in understanding gas solid reactions. Sorbed OH groups suggest that relative humidity can further influence the reactivity of gases on dust containing Fe₃O₄; the effect of relative humidity has been tested and is the subject of another study.³⁷

The atmospheric implications of these reactions are of particular relevance in polluted areas, where large emissions of anthropogenic dusts containing magnetite and mixtures of gases occur. Changes in the chemical composition of the dust particles can influence subsequent interactions such as the uptake of water vapour affecting nucleation processes leading to the formation of clouds (e.g., the size of the ice crystal) as well as the type and intensity of precipitation.

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