The effects of surfactants on the heterogeneous uptake of sulfur dioxide on hematite

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GRAPHICAL ABSTRACT
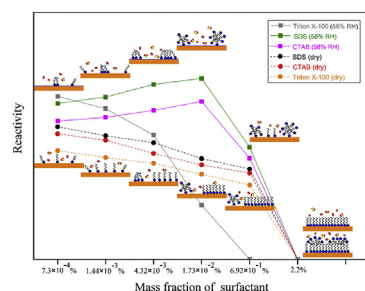
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ABSTRACT

Surfactants are often found to be associated with atmospheric particles. They can change the physicochemical properties of these particles, and thereby impact their chemical reactivity. However, their influences on heterogeneous reactions of atmospheric trace gases have not been paid much attention. In this study, the impacts of different surfactants on the heterogeneous conversion of SO_2 on hematite were investigated by using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), including cationic cetyltrimethylammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and nonionic polyethylene glycol tert-octylphenyl ether (Triton X-100). Results indicated that heterogeneous reactivities of hematite-surfactant mixtures were significantly different due to the presence of different surfactants. Under dry conditions, heterogeneous reactivities decreased with the increase of their concentrations, but the higher reactivities were observed at an appropriate concentration range of CTAB and SDS when compared to pure hematite, showing their promoting effects at this concentration range. Under the condition of 58% relative humidity, the heterogeneous reactivities increased first and then decreased with the increasing mass fractions of CTAB and SDS, but pure hematite showed the highest reactivity. While the mixtures containing Triton X-100 had stronger ability to suppress sulfate formation under 58% RH than under dry condition, though these mixtures under 58% RH presented same trend as under dry condition. Water molecules can renew surface reactive sites and promote sulfate formation at an appropriate mass fraction of CTAB or SDS, water molecules can also promote the adsorption mode transition of Triton X-100 from adsorption through terminal OH groups to adsorption through ethoxyl groups, resulting in more surface active sites being covered and a drastically decrease in the reactivity. A

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possible mechanism for the impact of surfactants on the heterogeneous conversion of SO_2 on hematite is proposed, and atmospheric implications based on these results are discussed.

1. 1Introduction

Surface active species or surfactants, known as amphiphilic molecules, are important contributors to the total organics found in atmospheric aerosols (Ahmed et al., 2016; Baduel et al., 2012; Feng et al., 2006; Gérard et al., 2016; Gill et al., 1983; Ho et al., 2001; Jaafar et al., 2018; Jimenez et al., 2009; Latif and Brimblecombe, 2004). These surfactants in atmospheric aerosols include various anionic, cationic and nonionic surfactants (Ahmed et al., 2016; Gérard et al., 2016; Kroflič et al., 2018; Latif and Brimblecombe, 2004). The primary sources of these surfactants are anthropogenic and biogenic emissions, as well as photochemical transformations of organic precursors. Among these sources, anthropogenic activities have contributed various surfactants to the surrounding environment due to the widespread applications of solubilizers, emulsifiers and detergents (Gérard et al., 2016), such as cationic, anionic and nonionic surfactants. These surfactants will be inevitably coated onto the atmospheric particles in various ways. Surfactant molecules can significantly affect interfacial properties and physicochemical properties of aerosol particles, which in turn have significant impacts on various atmospheric processes. For example, surfactants can affect the formation and growth of cloud condensation nuclei (CCN) through surface partitioning and surface tension reduction in activating droplets (Moore et al., 2011; Prisle et al., 2011). Surfactants also increase the lifetime of aerosol particles, fog droplets and cloud droplets, by inhibiting water vapor evaporation and reducing the efficiency with which these atmospheric components are scavenged (Gill and Graedel, 1983). Surfactants precipitating in aerosol particles can also cause an increase in light scattering, which would result in a larger negative radiative forcing than previously expected (Beaver et al., 2010). Moreover, surfactants can influence the heterogeneous processes of gaseous pollutants at different surfaces/interfaces (Donaldson et al., 2006). Liyana-Arachchi et al. found that the

adsorption of both naphthalene and ozone on surfactant-coated air/ice interface is enhanced when compared to bare air/ice interface (Liyana-Arachchi et al., 2012). Stemmler et al. investigated the effect of fatty acid surfactants on the uptake of nitric acid to deliquesced NaCl aerosol, and found that the uptake coefficient was reduced by a factor of 5–50 when the aerosol was coated with saturated linear fatty acids with carbon chain lengths of 18 and 15 atoms in monolayer quantities, while coatings with shorter saturated linear fatty acids with 12 and 9 carbon atoms and unsaturated oleic acid had no detectable effect on the rate of HNO_3 uptake. They believed that the formation of monolayer structures (highly ordered or less ordered films) determines their resistance to HNO_3 uptake (Stemmler et al., 2008). Park et al. reported that surfactants can control different gas transport and reactions at the surface of sulfuric acid in different ways. For example, surfactants can impose a barrier to N_2O_5 hydrolysis, be "invisible" to water evaporation, and even enhance gas uptake of HCl (Park et al., 2009). However, up to now, there have been only a few researches on the impacts of different surfactants on the heterogeneous reactions of trace gaseous atmospheric pollutants.

SO_2 is a major air pollutant and can be heterogeneously oxidized to sulfate aerosols on various particle surfaces (Ullerstam et al., 2003; Usher et al., 2003). The formed sulfate aerosols are known to have significant impacts on the global climate, environmental quality and human health. Meanwhile, the heterogeneous reactions of SO_2 are unavoidably affected by other species in the polluted atmosphere, and hence the heterogeneous conversion of SO_2 under the influence of other species has attracted much attention. For example, the heterogeneous conversion of SO_2 to sulfate can be promoted by NO_2 through the synergistic effects between NO_2 and SO_2 on different particle surfaces (Ma et al., 2008, 2017), which may account for the enhanced sulfate formation and the aggravation of severe haze pollution (Cheng et al., 2016; Xie et al., 2015). It has also been found that nitrate and its
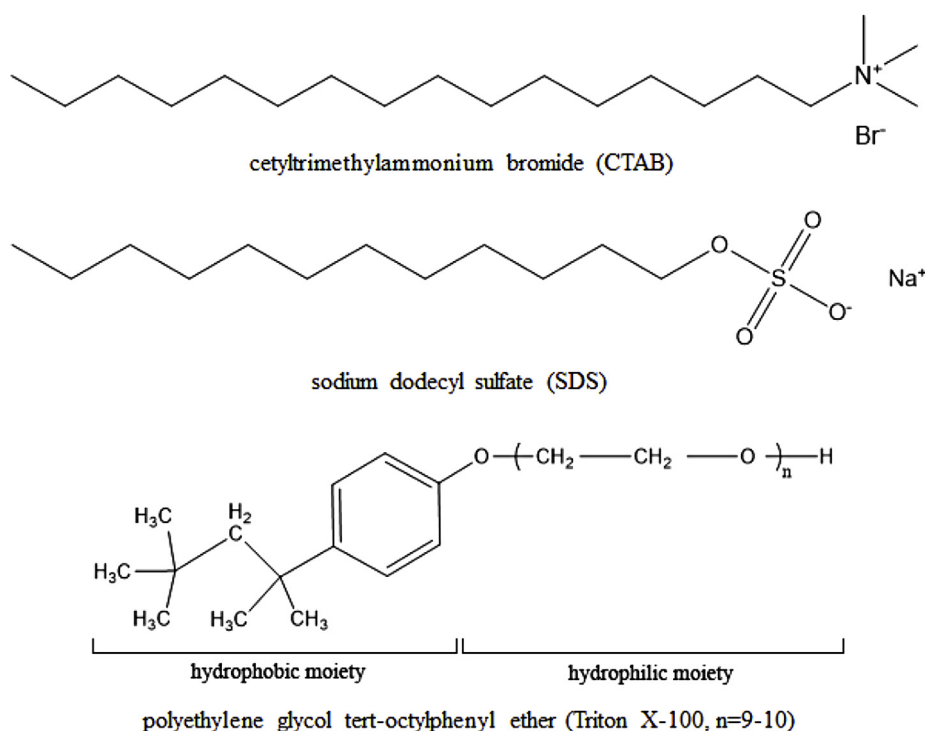
Scheme 1. Chemical structures of the surfactant molecules studied.

photolysis can promote the formation of sulfate during the heterogeneous reactions of SO_2 (Du et al., 2019; Gen et al., 2019; Kong et al., 2014). However, the heterogeneous conversion of SO_2 can be suppressed by the presence of CH_3CHO (Zhao et al., 2015), but not affected by the presence of formic acid (Wu et al., 2013). Although these studies indicate that the heterogeneous reactions of SO_2 are susceptible to different species, little attention has been paid to the impact of different surfactants on the heterogeneous reactions of SO_2 in laboratory studies up to now.

In this study, the impacts of different surfactants on heterogeneous conversion of SO_2 on mineral particle surfaces at room temperature were investigated by using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Hematite (α-Fe_2O_3, one of the typical components in mineral aerosol) and surfactants such as cationic cetyltrimethylammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and nonionic polyethylene glycol tert-octylphenyl ether (Triton X-100) were used as the model components of particles. To our knowledge, this is the first time that the impacts of different surfactants on heterogeneous conversion of SO_2 on mineral particle surfaces are reported. Through these investigations, we hope to gain insight into the mechanisms by which surfactants on hematite affect the conversion of SO_2 and the formation of sulfate, and also to provide useful information for atmospheric chemistry studies.

2. Experimental section

2.1. Chemicals

Hematite was prepared according to the procedure reported previously (Schwertmann and Cornell, 2000). Powder X-ray diffraction confirmed the prepared sample as pure hematite. The Brunauer-Emmett-Teller (BET) surface area was $19.6 \, m^2 \, g^{-1}$ (Micromeritics TriStar 3000, Micromeritics Instrument Co., USA.). Gaseous O_2, N_2 (99.999% purity, Shanghai Yunguang Specialty Gases Inc.), and SO_2 (97 ppm, SO_2/N_2, Shanghai Yunguang Specialty Gases Inc.) were introduced through an air dryer before use. Cationic cetyltrimethylammonium bromide (CTAB, $\geq$ 99.0% purity, Sigma-Aldrich), anionic sodium dodecyl sulfate (SDS, 99 + % purity, Sigma-Aldrich) and nonionic polyethylene glycol tert-octylphenyl ether (Triton® X-100, Sigma-Aldrich) were used without further purification. The chemical structures of the surfactant molecules studied are displayed in Scheme 1.

In order to systematically study the impacts of surfactants on heterogeneous reactions of SO_2, a series of hematite–surfactant mixtures with different mass fractions of surfactants in the mixtures were prepared, including 0%, 7.3×10^{-4}%, 1.44×10^{-3}%, 4.32×10^{-3}%, 1.728×10^{-2}%, 1.728×10^{-1}% and 6.921×10^{-1}%. In order to coat hematite by surfactant, for the mixtures containing CTAB or SDS,
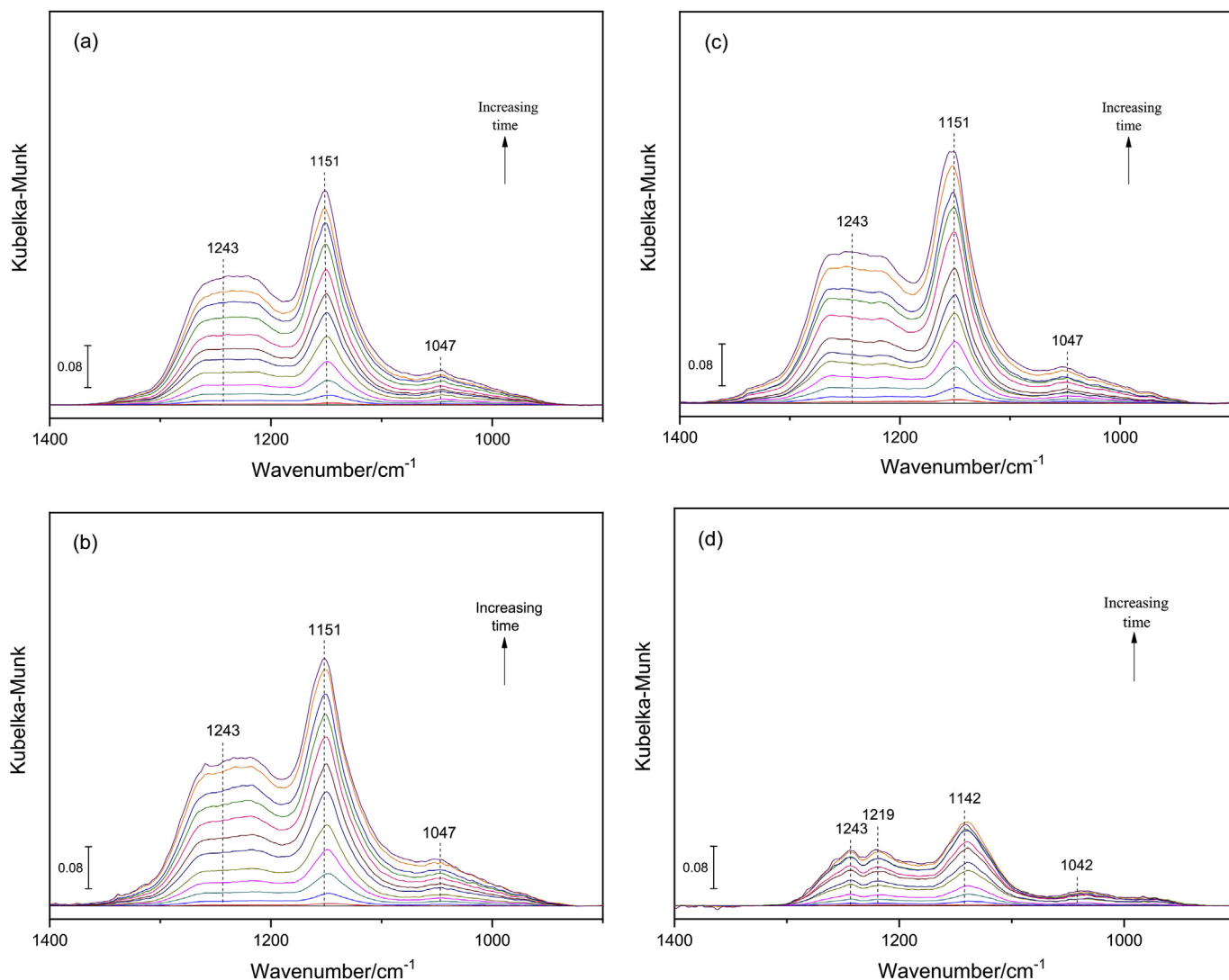

Fig. 1. DRIFTS spectra of surface products as a function of reaction time during the reactions of SO_2 with α-Fe_2O_3-surfactant mixtures (7.3×10^{-4}% of surfactant in the mixture) under dry conditions: (a) pure α-Fe_2O_3; (b) α-Fe_2O_3-CTAB; (c) α-Fe_2O_3-SDS; (d) α-Fe_2O_3-Triton X-100.

hematite was impregnated with a certain amount of aqueous solution of CTAB or SDS, respectively, and then the mixtures were stirred manually and dried under an infrared lamp. For the mixtures containing Triton X-100, hematite was impregnated with different concentrations of Triton X-100 solutions in n-hexane (ACS, > 99%, Aladdin Industrial Co.), and then the mixtures were blown by a nitrogen flow to remove n-hexane. All the prepared samples were stored in a desiccator at room temperature until further use.

2.2. In situ DRIFTS experiment

In situ DRIFTS experiments were performed by using a Nicolet Avatar 360 FTIR spectrometer, equipped with a high-sensitivity mercury cadmium telluride (MCT) detector and a Spectra-Tech diffuse reflectance accessory, as described previously (Kong et al., 2014). A 32 mg sample was placed into a ceramic crucible in the in situ chamber, and the temperatures of the chamber and sample were controlled by an automatic temperature controller. Before the reaction started, the reaction chamber and sample particles were purged with synthetic air (100 mLmin^{-1}) for 1 h, and then a background spectrum of the unreacted powder sample was collected. Subsequently, a mixture of SO$_2$ (3 ppm) and O$_2$ (21% v/v) with nitrogen as a carrier gas was introduced into the chamber at a total flow rate of 100 mLmin^{-1}, and then IR spectra were collected as a function of reaction time. All the spectra reported here were recorded at a resolution of 4 cm^{-1} for 100 scans. Each experiment of certain surfactant concentration sample was repeated three times under the same experiment conditions. In addition, considering that atmospheric heterogenous reactions often occur at a certain relative humidity (RH) and the surface-adsorbed water plays an important role in the heterogeneous chemistry of atmospheric SO$_2$, the DRIFTS experiments at relative humidity of 58% were also performed. The relative humidity of 58% was obtained by regulating the mixing ratio between a water-saturated nitrogen flow and a dry nitrogen flow, using mass flow controllers. The water-saturated nitrogen flow was provided by bubbling a nitrogen flow through water in a humidifier kept at room temperature.

3. Results and discussion

3.1. Effect of surfactant on surface species formed from the uptake of SO$_2$ onto hematite under dry condition

In situ DRIFTS experiments were carried out on pure hematite and a series of hematite-surfactant mixtures with the surfactant mass fractions of 0%, 7.3×10^{-4}%, 1.44×10^{-3}%, 4.32×10^{-3}%, 1.728×10^{-2}%, 1.728×10^{-1}% and 6.921×10^{-1}% under dry and 58% RH conditions, respectively. Each experiment was performed at 298 K with 32 mg of sample to investigate the effects of surfactants on the uptake of gas-phase SO$_2$ onto the sample particle surface and the nature of the formed surface-bound species.

3.1.1. Surface sulfur-containing species and hydroxyl group

Fig. 1 shows the in situ DRIFT spectra (1400–900 cm^{-1}) of surface species as a function of reaction time during the reactions of SO$_2$ with pure α-Fe$_2$O$_3$ and α-Fe$_2$O$_3$-surfactant mixtures (7.3×10^{-4}% of surfactant in each mixture) under dry condition. Fig. 1a–d represent the spectra obtained from four particle samples, including pure α-Fe$_2$O$_3$ (Fig. 1a), α-Fe$_2$O$_3$-CTAB mixture (Fig. 1b), α-Fe$_2$O$_3$-SDS mixture (Fig. 1c) and α-Fe$_2$O$_3$-Triton X-100 mixture (Fig. 1d), respectively. As can be seen from Fig. 1a, a prominent peak at 1151 cm^{-1}, a broad shoulder peak at 1243 cm^{-1} and a weak peak at 1047 cm^{-1} are readily observed in the spectra. The intensities of these peaks increase as the reaction proceeds. According to previous studies (Fu et al., 2007; Kong et al., 2014; Sugimoto and Wang, 1998; Wu et al., 2013; Yang et al., 2017), these peaks can be assigned to adsorbed bisulfate and/or sulfate on the particle surface. That is, the peak at around 1243 cm^{-1} is

attributed to free SO$_4^{2-}$, the peak at 1151 cm^{-1} is assigned to adsorbed bidentate SO$_4^{2-}$, and the peak at 1047 cm^{-1} is attributed to bridging SO$_4^{2-}$/HSO$_4^-$. These results indicate the formation of adsorbed sulfates. The most apparent peak at 1151 cm^{-1} indicates that the adsorbed bidentate SO$_4^{2-}$ is the dominant oxidation product. In addition, the broad peak around 1243 cm^{-1} in Fig. 1a actually contains two major peaks at 1261 and 1219 cm^{-1}. The increase in peak intensity at 1219 cm^{-1} with the increase in exposure time indicates increased surface acidity (Kong et al., 2014), which can also be supported by the appearance of a slowly increasing broad peak extending from 3600 to 2500 cm^{-1} since this broad peak is primarily associated with the O–H vibration of hydrogen-bonded OH groups of acidic species (not shown here) (Finlayson-Pitts et al., 2003; Goodman et al., 1999; Nanayakkara et al., 2012). Under other conditions, the similar results shown in Fig. 1b–d are obtained, indicating that adsorbed sulfates are still the main products during the heterogeneous reactions of SO$_2$ on the surfaces of the α-Fe$_2$O$_3$-surfactant mixtures. However, a red shift (≈ 9 cm^{-1}) of the peak assigned to adsorbed bidentate SO$_4^{2-}$, together with a concomitant red shift (≈ 5 cm^{-1}) of the peak attributed to bridging SO$_4^{2-}$/HSO$_4^-$ has been observed for the uptake of SO$_2$ on the α-Fe$_2$O$_3$-Triton X-100 mixture. No red shifts of the two peaks have been observed on the α-Fe$_2$O$_3$-CTAB and α-Fe$_2$O$_3$-SDS mixtures. Triton X-100 has a chemical structure consisting of hydrophobic t–C$_8$H$_{17}$–C$_6$H$_4$- and hydrophilic -(OCH$_2$CH$_2$)$_{10}$OH (Scheme 1), and its adsorption mode on hydrophilic particle surfaces remains controversial (Chen et al., 1998; Nevskaia et al., 1995). However, the adsorption of Triton X-100 takes place whether through the ethoxyl groups or through the terminal OH groups on the hematite surface (Chen et al., 1998; Nevskaia et al., 1995), and this observation implies the occurrence of the interaction between oxygen atoms in hydrophilic moiety of Triton X-100 and surface sulfate species. Moreover, Triton X-100 has the largest molecular weight among the three kinds of surfactants, and hence at the same mass fraction of surfactant and mixture mass the least Triton X-100 molecules are adsorbed on the particle surfaces. However, the α-Fe$_2$O$_3$-Triton X-100 mixture has the lowest reactivity at the same mass fractions of surfactant among the three different surfactant mixtures, showing strong inhibition ability of Triton X-100 against SO$_2$ conversion. This result indicates that Triton X-100 not only has a similar influence mechanism on SO$_2$ heterogeneous conversion to CTAB or SDS, but also has a different impact on SO$_2$ heterogeneous conversion, suggesting the different adsorption modes of Triton X-100 on α-Fe$_2$O$_3$ surfaces. That is, this result further demonstrates the occurrence of the adsorption of Triton X-100 on the hematite surface through its ethoxyl groups and terminal OH groups.

It should be pointed out that some differences in intensity are shown in Fig. 1b–d when compared to Fig. 1a. The intensities of the characteristic peaks of surface adsorbed sulfate in Fig. 1a are lower than those in Fig. 1b and c but higher than that in Fig. 1d. This result clearly indicates that the CTAB and SDS surfactants with a mass fraction of 7.3×10^{-4}% in the mixtures promote the heterogeneous conversion of SO$_2$ and the formation of adsorbed sulfates on the dry particles to some extent, while the Triton X-100 surfactant with the same mass fraction in the mixture suppresses the heterogeneous conversion of SO$_2$ and the formation of adsorbed sulfates on the dry particles to a certain extent.

In addition, compared to those negative peaks appeared on the pure α-Fe$_2$O$_3$, the same negative peaks at 3661 and 3631 cm^{-1} are observed on the α-Fe$_2$O$_3$-surfactant mixtures, and their intensities increase with the increase of time, implying their consumption as the reaction proceeds. These negative peaks are attributed to the surface hydroxyl groups bonded to the surface iron species of octahedral and tetrahedral sites, respectively (Watanabe et al., 1994), which implies that surface OH groups are involved in the reaction and are the reaction active sites for SO$_2$ even in the presence of a small amount of surfactants (Goodman et al., 2001; Kong et al., 2014).

Finally, it is noteworthy that no apparent absorption peaks associated with surfactants are observed, indicating that surfactants

themselves do not degrade or decompose during the heterogeneous reaction of SO_2.

3.1.2. Comparison of heterogeneous conversion of SO_2 on hematite–surfactant mixtures with different mass fractions of surfactants under dry condition

In order to further investigate the influences of different surfactants and their different mass fractions on sulfate formation, the amount of the formed sulfate is compared in this study. Fig. 2 shows the variations of total integrated absorbance areas of the formed adsorbed sulfate species as a function of reaction time during the heterogeneous reactions of SO_2 on α-Fe_2O_3 particles with and without surfactants. Overall, the formation of sulfate shown in Fig. 2 slowly increases as reaction proceeds under the influence of different surfactants, indicating that the heterogeneous conversion of SO_2 still occurs within the given range of surfactant concentrations in this study, except that excessive concentrations of surfactants (e.g. 2.2%) completely inhibit the reaction. Furthermore, if the reaction occurring on pure α-Fe_2O_3 is excluded, overall the presence of the three different types of surfactants has an obvious inhibition effect on the formation of sulfate, which shows an obvious downward trend in sulfate formation with the increase of their concentrations in the mixtures. To be specific, Fig. 2a and b indicate that the presence of a small amount of CTAB (7.3×10^{-4}% and 1.44×10^{-3}%) and SDS (7.3×10^{-4}%, 1.44×10^{-3}% and 4.32×10^{-3}%) can significantly promote SO_2 conversion and sulfate production to a certain extent when compared to pure α-Fe_2O_3, but with the further increase in the concentrations of these surfactants in the mixtures, the promotion effect on the reaction is weakened and the sulfate production shows a downward trend. It confirms that the presence of a larger amount of surfactants in the mixtures suppresses the heterogeneous uptake of SO_2 and further oxidation to sulfate on the particles. As for the α-Fe_2O_3-Triton X-100 mixtures, it can be noted that all the provided mass ratios of this surfactant (7.3×10^{-4}%–2.2%) in the mixtures invariably suppress the formation of sulfate, which exhibits the corresponding tendency to decrease with the increase of its concentration in the mixtures (Fig. 2c).

3.2. Effect of relative humidity on the heterogeneous uptake of SO_2 on the α-Fe_2O_3-surfactant mixtures

3.2.1. Surface sulfur-containing species

Previous studies have demonstrated relative humidity plays an important role in the heterogeneous oxidation of SO_2 (Liu et al., 2018; Zhang et al., 2018; Yang et al., 2017). In this work, the effect of RH on heterogeneous reactions of SO_2 on pure hematite and three kinds of hematite-surfactant mixtures was investigated. The collected in situ
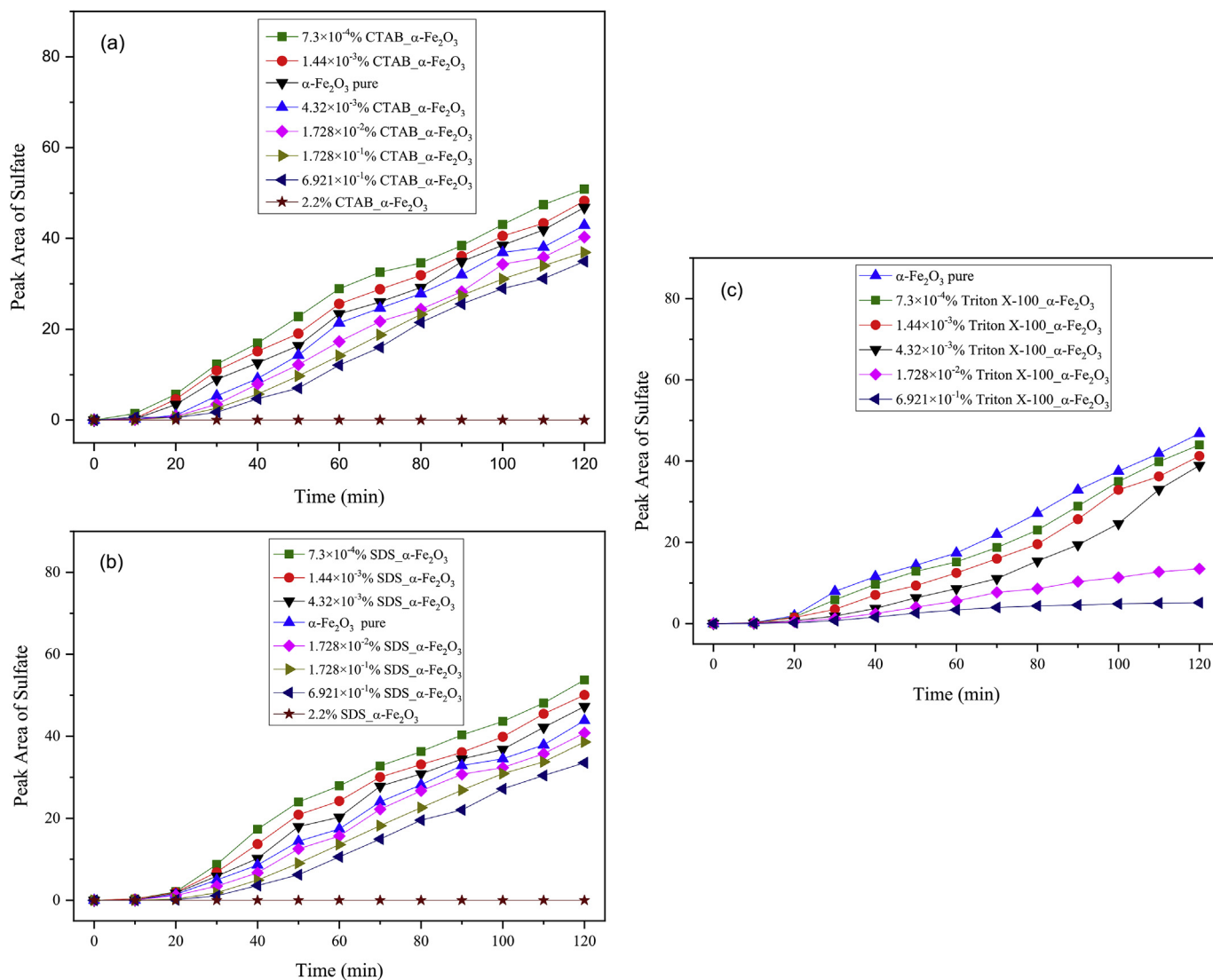

Fig. 2. Comparison of integrated peak areas of the formed sulfate species as a function of reaction time during the reactions of SO_2 with hematite-surfactant mixtures of different mass ratios in dry condition: (a) α-Fe_2O_3-CTAB; (b) α-Fe_2O_3-SDS; (c) α-Fe_2O_3-Triton X-100.

DRIFTS spectra (1400–900 cm^{-1}) of the heterogeneous reactions of SO$_2$ on the surfaces of pure α-Fe$_2$O$_3$ (Fig. 3a), α-Fe$_2$O$_3$-CTAB (Fig. 3b), α-Fe$_2$O$_3$-SDS (Fig. 3c) and α-Fe$_2$O$_3$-Triton X-100 (Fig. 3d) at 58% RH were shown in Fig. 3. The mass fraction of different surfactants in the α-Fe$_2$O$_3$-surfactant mixtures (7.3 × 10^{-4}% of surfactant in the mixture) is the same as those in Fig. 1. As can be seen from Fig. 3, a prominent peak at 1148 cm^{-1}, a broad shoulder peak at around 1200 cm^{-1} and two weak peaks at 1047 and 976 cm^{-1} are observed in the spectra, indicating that adsorbed bisulfate and/or sulfate formed on the particle surfaces (Kong et al., 2014; Sugimoto and Wang, 1998; Wu et al., 2013; Yang et al., 2017). This result is similar to that collected under dry conditions. Moreover, it is evident that enhanced sulfate formation on the particle surfaces is observed when compared to that under dry conditions due to the influence of RH, especially on the α-Fe$_2$O$_3$-Triton X-100 mixtures, implying that at this surfactant concentration water can promote the formation of adsorbed sulfates to some extent.

In addition, compared to that under dry conditions, the red shift of the peak assigned to adsorbed bidentate SO$_4^{2-}$ remains, but the red shift of the peak attributed to bridging SO$_4^{2-}$/HSO$_4^-$ disappears, indicating that the presence of water molecules weakens the interaction between oxygen atoms in hydrophilic moiety of Triton X-100 and surface bridging sulfate species. Water molecules can readily hydrogen-bond to surface hydroxyl groups, surface adsorbed sulfate species and

oxygen atoms in hydrophilic moiety of Triton X-100. This result may imply that water molecules replace surfactants and further interact with surface bridging sulfate species and oxygen atoms in hydrophilic moiety of Triton X-100, avoiding the competition between α-Fe$_2$O$_3$ and surfactant for the formed sulfate species and thereby restoring the adsorption mode of the surface bridging sulfate species similar to those formed on pure α-Fe$_2$O$_3$ (Alexeev et al., 1996).

3.2.2. Comparison of heterogeneous conversion of SO$_2$ on hematite–surfactant mixtures with different mass fractions of surfactants under 58% RH conditions

Fig. 4 shows the integrated peak areas of the formed sulfate species as a function of the reaction time during the heterogeneous reactions of SO$_2$ on the surfaces of pure α-Fe$_2$O$_3$, α-Fe$_2$O$_3$-CTAB, α-Fe$_2$O$_3$-SDS and α-Fe$_2$O$_3$-Triton X-100 mixtures under 58% RH conditions. It is evident that the reactivities of the mixture samples vary with mass fractions of surfactants. The α-Fe$_2$O$_3$-CTAB and α-Fe$_2$O$_3$-SDS mixtures upon exposure to SO$_2$ under 58% RH conditions show different reactivity of SO$_2$ oxidation but similar changes in reactivity. That is, their reactivity firstly increases with the increase of mass fraction of surfactants in the mixtures from 7.3 × 10^{-4}% to 1.728 × 10^{-2}%, and then decreases with the increasing mass fraction of surfactants from 1.728 × 10^{-2}% to 6.912 × 10^{-1}%. No reactivity is found when the mass fraction of

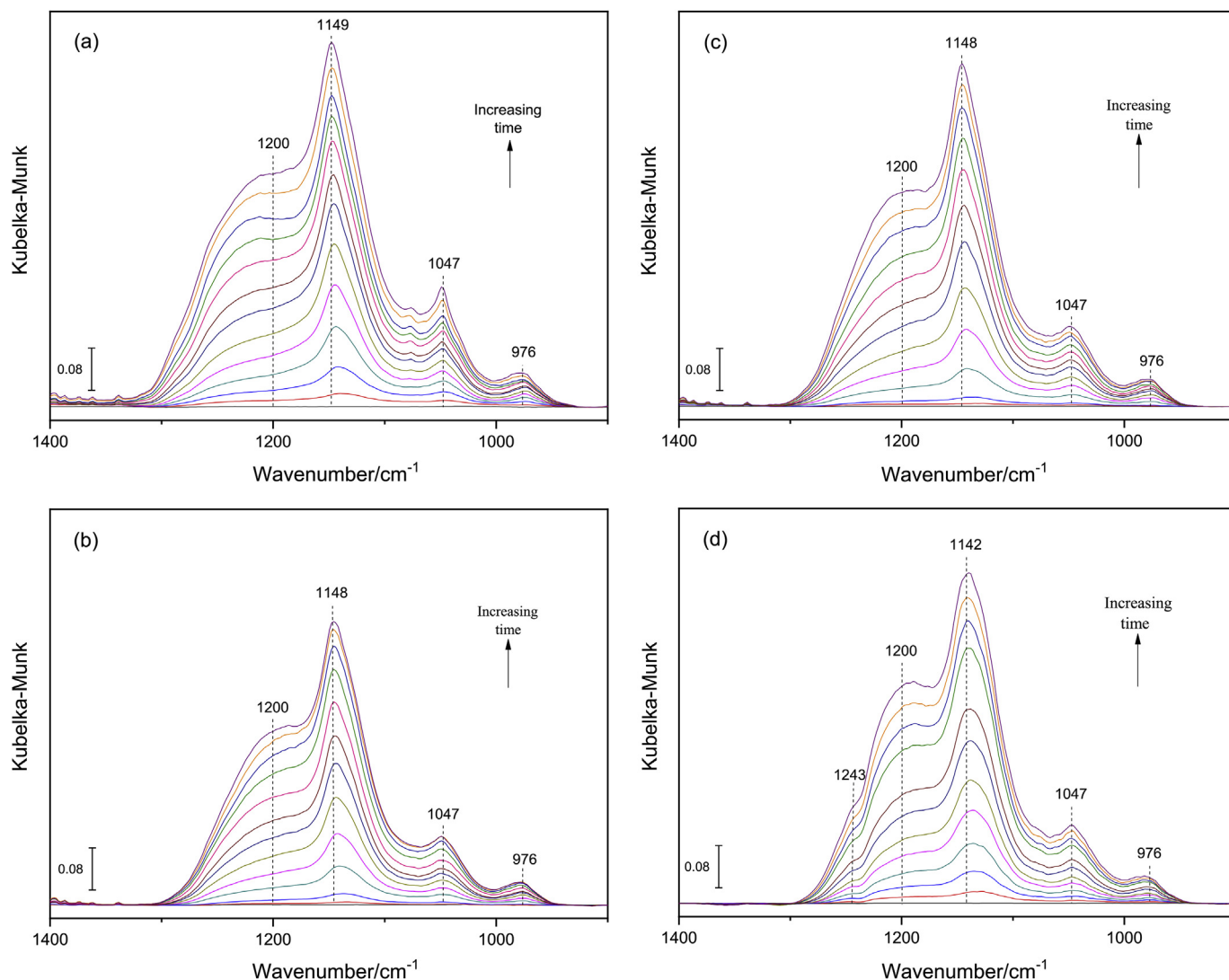**Fig. 3.** DRIFTS spectra of surface products as a function of reaction time during the reactions of SO$_2$ with hematite-surfactant mixtures (7.3 × 10^{-4}% of surfactant in the mixture) at 58% RH: (a) pure hematite; (b) hematite-CTAB; (c) hematite-SDS; (d) hematite-Triton X-100.
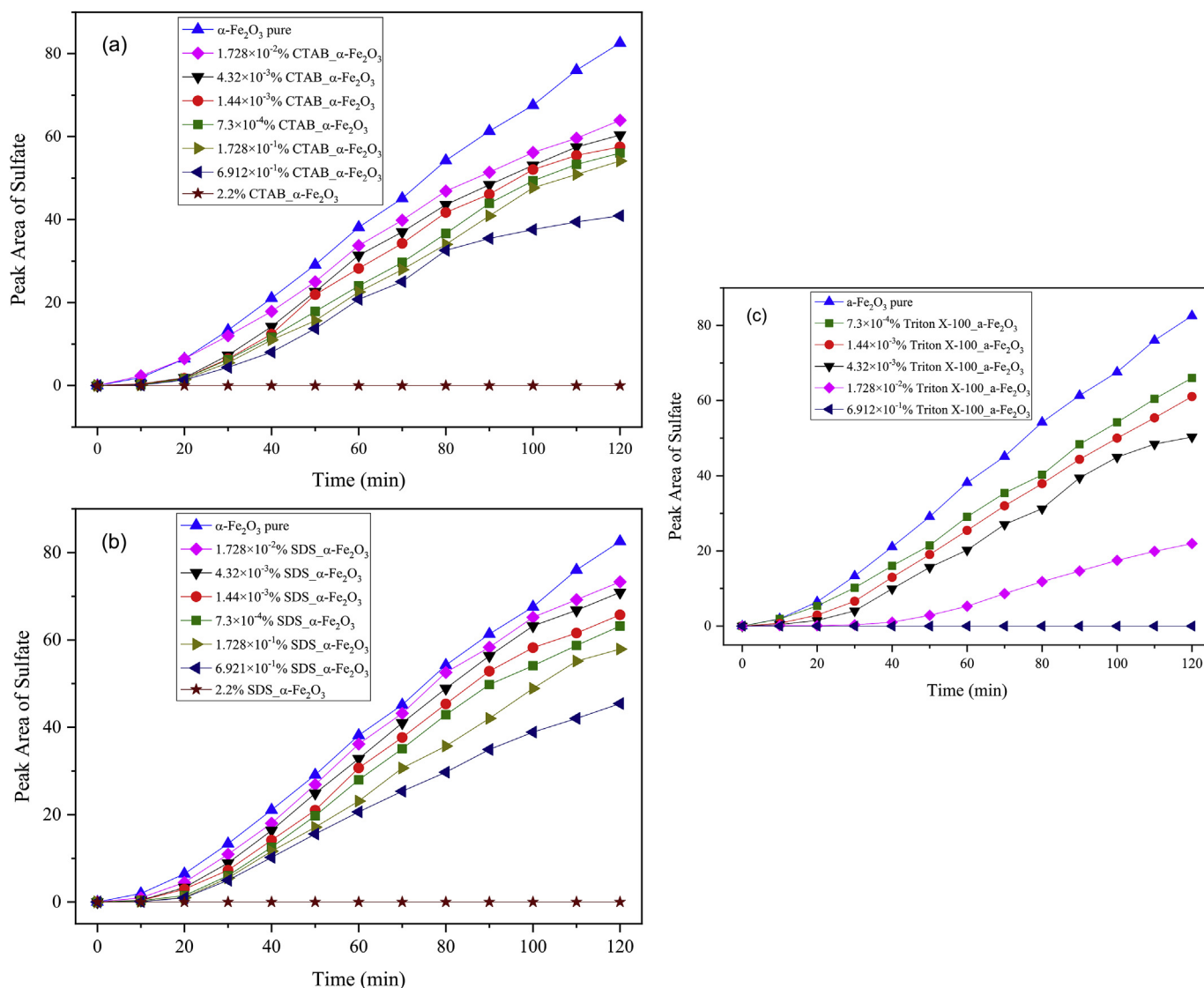
Fig. 4. Comparison of integrated peak areas of the formed sulfate species as a function of reaction time during the reactions of SO_2 with hematite-surfactant mixtures of different mass ratios at 58% RH: (a) Fe_2O_3-CTAB; (b) Fe_2O_3-SDS; (c) Fe_2O_3-Triton X-100.

surfactants increases to 2.2%. However, the reactivities of α-Fe_2O_3-Triton X-100 mixture samples demonstrate a stable tendency to decrease with the increase of mass fraction of the surfactant from 7.3×10^{-4}% to 6.912×10^{-1}% in the samples. It should be pointed out that pure α-Fe_2O_3 shows the highest reactivity under 58% RH conditions, though both CTAB and SDS at an appropriate range of mass fractions in the mixtures and water molecules can promote SO_2 heterogeneous oxidation, which is quite different from those observed under dry conditions.

α-Fe_2O_3 particle surfaces possess abundant Lewis acid sites, hydroxyl groups, and oxygen vacancies (Watanabe et al., 1994; Watanabe and Seto, 1993). Generally, a large amount of active sites on pure α-Fe_2O_3 particle surfaces is available for SO_2 at the early reaction stage (Yang et al., 2017). SO_2 is a 1,3-dipolar molecule. The heterogeneous conversion of SO_2 on α-Fe_2O_3-surfactant mixture particle surfaces will be influenced by the coverage of surface reactive sites and the attraction of polar particle surface to SO_2 and H_2O, as well as the repulsion of non-polar group of the surfactant to SO_2 and H_2O. The changed polarity of particle surface mainly originates from the adsorbed polar head of surfactants and can be modified by surfactant adsorption. The reactive sites are not only primary adsorption sites for surfactants but also important reaction active sites for the heterogeneous conversion of SO_2

(Baltrusaitis et al., 2007; Goodman et al., 2001). Therefore, the adsorption of surfactants on the surface of α-Fe_2O_3 will affect these sites available for the heterogeneous oxidation of SO_2, and thereby influence the heterogeneous reactivity of the mixtures. Meanwhile, under low surface coverage, the electrostatic attraction of the polar groups of the surfactants will facilitate the diffusion of SO_2 and H_2O to the reactive surface, and thus promote the heterogeneous conversion of SO_2, whereas the repulsion of non-polar groups of the surfactants to polar molecules SO_2 and H_2O will lead to the opposite result.

On the other hand, the average minimum molecular surface area (A_{min}) occupied by one surfactant molecule in surface monomolecular layer has been reported by previous studies (Alexeev et al., 1996; El-Aila, 2009; Jañczuk et al., 1995; Nakahara et al., 2011). For example, the A_{min} values for CTAB, SDS and Triton X-100 are reported to be 63 ($\times 10^{-20}$ m^2), 53 ($\times 10^{-20}$ m^2) and 68 ($\times 10^{-20}$ m^2), respectively (El-Aila, 2009). Hence, the saturation value of the surfactant adsorption in the adsorption monomolecular layer is roughly estimated from these data based on the measured BET surface area of pure α-Fe_2O_3. The calculated saturation values in this study for CTAB, SDS and Triton X-100 are 1.88×10^{-2} g, 1.77×10^{-2} g and 3.10×10^{-2} g per gram of α-Fe_2O_3, respectively, which correspond to the mass fractions of 1.85%, 1.74% and 3.00%, respectively. Therefore, except for α-Fe_2O_3-CTAB

and α-Fe₂O₃-SDS mixtures with the mass fraction of 2.2%, the other mass fractions of different surfactants in the mixtures studied in this study do not meet the saturation coverage. For the α-Fe₂O₃-CTAB and α-Fe₂O₃-SDS mixtures with the mass fraction of 2.2%, surfactant monolayer or hemimicelles on the monolayer would be formed on the hydrophilic α-Fe₂O₃ surfaces (Tyrode et al., 2008), which would not only cover and occupy the reaction active sites on α-Fe₂O₃ surfaces but also act as a barrier for gaseous 1,3-dipolar molecules SO₂ and water molecules to transport across the interface, inhibiting SO₂ uptake and sulfate formation on α-Fe₂O₃ surfaces. For the α-Fe₂O₃-surfactant mixtures with low mass fractions, the low mass fractions correspond to the unsaturated surface coverage. According to the previous study (Tyrode et al., 2008), at a very low coverage, the hydrocarbon chains of the adsorbed surfactants may be randomly distributed on particle surfaces. As the coverage increases, the surfactant molecules may be further randomly distributed on particle surfaces, which will further increase the coverage of surface reactive sites. When the surface coverage increases to a certain extent, interactions between adsorbed surfactant molecules may lead to the formation of some islands or hemimicelles or admicelles rather than coating the surface evenly (Garland et al., 2008; Tyrode et al., 2008), which may lead to the recovery of some surface reactive sites. All the cases mentioned above will lead to the existence of some reactive regions such as microregions and microchannels for SO₂ uptake, and overall the number of these regions firstly increases and then decreases with the increase of surfactant mass fraction in the mixtures. Therefore, for the observed phenomena under unsaturated coverage on α-Fe₂O₃-CTAB and α-Fe₂O₃-SDS mixtures, that is, the mixture reactivities firstly increase and then decrease with the increase of surfactant mass fraction under 58% RH conditions, the possible reason is that, with the surfactant mass fraction increasing, more and more active sites are covered by surfactant molecules, which leads to fewer and fewer reactive regions and thus decreases the reactivity. When the mass fraction of surfactants increases to a certain range, the islands, hemimicelles or admicelles on the hydrophilic α-Fe₂O₃ surfaces are gradually formed, which alters the adsorption mode of surfactants and leads to the appearance and recovery of more reactive microregions or microchannels. Meanwhile, the formation of islands, hemimicelles or admicelles with polar head groups being out is also conductive to gaseous SO₂ and H₂O transport. Both favor the conversion of SO₂ and the formation of adsorbed sulfate, leading to the increased reactivity. Further increase in the mass fraction of surfactants will result in further reduction of the reactive regions, which hinders the SO₂ oxidation and leads to low reactivity again. However, no similar phenomenon is observed on α-Fe₂O₃-Triton X-100 mixtures. This result clearly indicates that the adsorption behavior of Triton X-100 on α-Fe₂O₃ is different from those of CTAB and SDS, revealing that the adsorption of Triton X-100 on the hematite surface may take place not only through its terminal OH groups but also through its ethoxyl groups. This is consistent with that discussed earlier. While at high coverages, monolayer, hemimicelles on a monolayer, bilayer or more admicelles may be formed on particle surfaces (Tyrode et al., 2008), which will inhibit SO₂ and water molecules to access to the particle surfaces. These may be the reasons why α-Fe₂O₃-CTAB and α-Fe₂O₃-SDS mixtures with mass fraction of 2.2% have no reactivities but others and α-Fe₂O₃-Triton X-100 mixtures have.

In addition, the amounts of the formed sulfate under dry and 58% RH conditions are compared. Fig. 5 shows the variations of total integrated absorbance areas of formed sulfate as a function of the mass fraction of surfactants during the uptake of SO₂ on the hematite-surfactant mixtures under the dry and 58% RH conditions. As can be seen from Fig. 5, for the α-Fe₂O₃-CTAB and α-Fe₂O₃-SDS mixtures, the formation of adsorbed sulfate increases first and then decreases under 58% RH conditions with the increasing surfactant mass fraction, while under dry conditions, the formation of adsorbed sulfate decreases with the increasing surfactant mass fraction. The amount of the formed sulfate under 58% RH conditions is higher than that under dry conditions,

indicating that the presence of water can promote the formation of sulfate. Furthermore, this result clearly demonstrates that water molecules can enhance surface ionic mobility, promote the formation of more and more islands or hemimicelles or admicelles (Tyrode et al., 2008), and then renew more and more surface reactive sites when the mass fraction of surfactants increases from $7.3 \times 10^{-4}\%$ to $1.728 \times 10^{-2}\%$. While with the further increase of the mass fraction of surfactants, this effect of water molecules cannot be easily observed. This suggests that water molecules have a significant impact on the formation of sulfate during the heterogeneous conversion of SO₂. In addition, the formation of adsorbed sulfates on α-Fe₂O₃-SDS mixtures is always higher than that on α-Fe₂O₃-CTAB mixtures with the increasing surfactant mass fraction whether under dry conditions or under 58% RH conditions. One possible explanation is that SDS has shorter hydrophobic groups than CTAB.

For the α-Fe₂O₃-Triton X-100 mixtures, under dry conditions, the formation of adsorbed sulfates decreases with the increasing surfactant mass fraction, and the overall trend is similar to those of CTAB and SDS. Under 58% RH conditions, the formation of adsorbed sulfate drastically decreases with the increasing surfactant mass fraction, revealing that the α-Fe₂O₃-Triton X-100 mixture shows a completely different reaction behavior from CTAB and SDS, and the behavior is also completely different from that under dry conditions. Compared to that under dry conditions, this result verifies that water molecules promote the adsorption mode transition of Triton X-100 from the adsorption through the terminal OH groups to the adsorption through the ethoxyl groups. This will result in more surface active sites being covered, and consequently lead to a drastically decrease in reactivity.

3.3. Proposed mechanism for SO₂ uptake on hematite–surfactant mixtures

According to the above experimental results and discussion, the surfactants themselves do not degrade or decompose during the heterogeneous reaction of SO₂, and they affect the heterogeneous conversion of SO₂ and the formation of sulfate mainly through the occupancies of active sites, the modifications of α-Fe₂O₃ surface properties and the changes of adsorption modes, especially, the changed adsorption modes by their self-assembly. Therefore, even though the heterogeneous reactivities are obviously different among the α-Fe₂O₃-surfactant mixtures with different mass fractions, the reaction mechanisms of SO₂ on these mixture samples should be the same as that reported
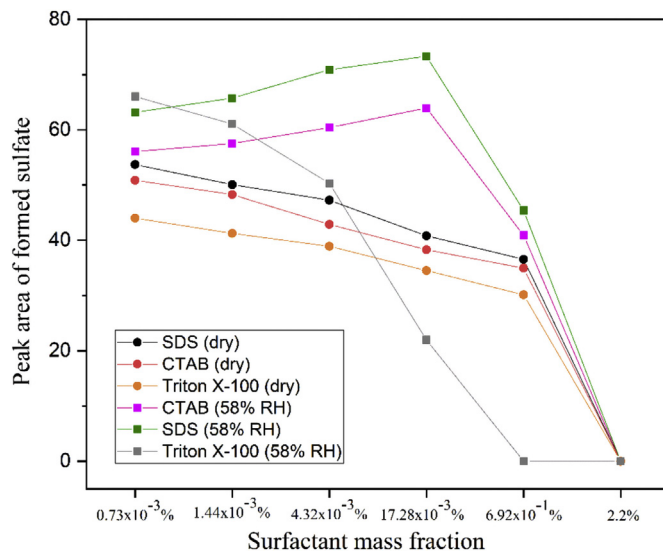
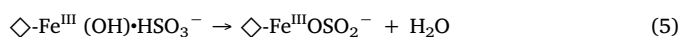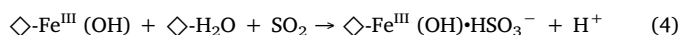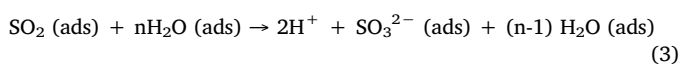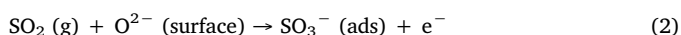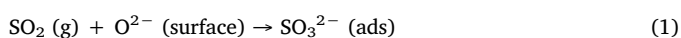**Fig. 5.** Comparison of integrated peak areas of formed sulfate species during the uptake of SO₂ on hematite-surfactant mixtures with different mass ratios under the dry and 58% RH conditions.
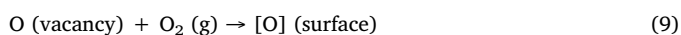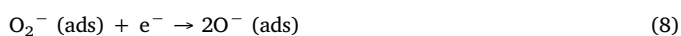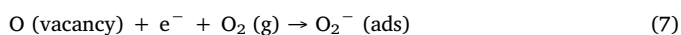
previously (Goodman et al., 2001; Baltrusaitis et al., 2007; Fu et al., 2007; Yang et al., 2017). In addition, water plays an important role in the atmospheric heterogeneous reactions (Yang et al., 2017). In this study, the experiments were performed under dry and 58% RH conditions. However, adsorbed water molecules still remain on the dry sample surfaces because the particle samples haven't been undergone any high temperature and high vacuum treatment. Meanwhile, Ma et al. found that about 1–5 layers of surface water were adsorbed on α-Fe_2O_3 at 20%–90% RH (Ma et al., 2010), and thus several limited adsorbed water layers will be present on the sample surfaces under 58% RH conditions (Baltrusaitis et al., 2007; Ma et al., 2010). The sample in our experiment was still loose powder rather than being immersed in a solution under the condition of 58% RH. DRIFTS spectra for those under 58% RH condition demonstrated the promoting effect of surface-adsorbed water on the formation of adsorbed sulfates (not solvated sulfates), which not only indicates that the adsorbed water will favor the adsorption of SO_2 and the formation of sulfate species (Yang et al., 2017), but also further reveals that the reactions involved are not heterogenous aqueous reactions. Therefore, the proposed mechanism is discussed below.
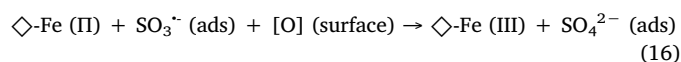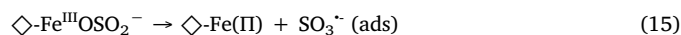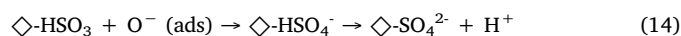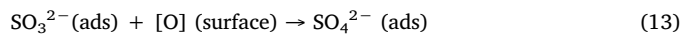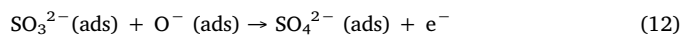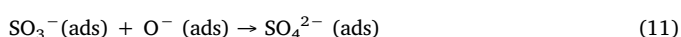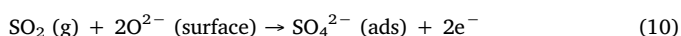
Adsorbed sulfate formation involves SO_2 adsorption, sulfite species formation and their subsequent oxidation. Previous studies of SO_2 adsorption on metal oxides have shown that surface oxygen sites [O^{2-}(surface)], hydroxyl groups ($\Diamond$-Fe^{III}(OH), $\Diamond$-OH) and oxygen vacancies [O(vacancy)] can play important roles in SO_2 adsorption and sulfate formation (Baltrusaitis et al., 2007; Fu et al., 2007; Goodman et al., 2001; Yang et al., 2017). The consumption of hydroxyl groups has been discussed earlier. The adsorption and dissociation of water molecules on α-Fe_2O_3 surfaces result in the formation of hydroxyl groups (Baltrusaitis et al., 2007; Yang et al., 2017). α-Fe_2O_3 is in fact oxygen deficient (Warschkow et al., 2002), and oxygen vacancies are inevitably present on α-Fe_2O_3 surfaces (Atkinson et al., 2003). Accordingly, in this study, the formation of adsorbed sulfite species could proceed via the following reactions of some of the surface sites with SO_2 (Baltrusaitis et al., 2007; Fu et al., 2007; Goodman et al., 2001; Yang et al., 2017). Additionally, the dissociated of adsorbed SO_2 in limited water layers could also produce sulfite species (Yang et al., 2017).

$$SO_2 \text{ (g)} + O^{2-} \text{ (surface)} \rightarrow SO_3^{2-} \text{ (ads)} \tag{1}$$

$$SO_2 \text{ (g)} + O^{2-} \text{ (surface)} \rightarrow SO_3^{-} \text{ (ads)} + e^{-} \tag{2}$$

$$SO_2 \text{ (ads)} + nH_2O \text{ (ads)} \rightarrow 2H^{+} + SO_3^{2-} \text{ (ads)} + \text{(n-1)} H_2O \text{ (ads)} \tag{3}$$

$$\Diamond\text{-}Fe^{III} \text{ (OH)} + \Diamond\text{-}H_2O + SO_2 \rightarrow \Diamond\text{-}Fe^{III} \text{ (OH)} \cdot HSO_3^{-} + H^{+} \tag{4}$$

$$\Diamond\text{-}Fe^{III} \text{ (OH)} \cdot HSO_3^{-} \rightarrow \Diamond\text{-}Fe^{III}OSO_2^{-} + H_2O \tag{5}$$

$$\Diamond\text{-OH} + SO_2 \rightarrow \Diamond\text{-}HSO_3 \tag{6}$$

On the other hand, O(vacancy) sites have been shown to be primary adsorption sites for molecular oxygen, resulting in the formation of active oxygen [O^{-} (ads)] or [O] (surface) (Baltrusaitis et al., 2007; Al-Mashta et al., 1982; Yang et al., 2017).

$$O \text{ (vacancy)} + e^{-} + O_2 \text{ (g)} \rightarrow O_2^{-} \text{ (ads)} \tag{7}$$

$$O_2^{-} \text{ (ads)} + e^{-} \rightarrow 2O^{-} \text{ (ads)} \tag{8}$$

$$O \text{ (vacancy)} + O_2 \text{ (g)} \rightarrow [O] \text{ (surface)} \tag{9}$$

The formed sulfite species would be oxidized by surface reconstruction of SO_3^{2-} (ads), electron transfer between SO_2 and O^{2-} (surface)(10), active oxygen oxidation (11)–(14), and a series of radical reactions to form sulfate or bisulfate (15) and (16) (Al-Mashta et al., 1982; Baltrusaitis et al., 2007; Fu et al., 2007; Yang et al., 2016, 2017).

$$SO_2 \text{ (g)} + 2O^{2-} \text{ (surface)} \rightarrow SO_4^{2-} \text{ (ads)} + 2e^{-} \tag{10}$$

$$SO_3^{-} \text{(ads)} + O^{-} \text{ (ads)} \rightarrow SO_4^{2-} \text{ (ads)} \tag{11}$$

$$SO_3^{2-} \text{(ads)} + O^{-} \text{ (ads)} \rightarrow SO_4^{2-} \text{ (ads)} + e^{-} \tag{12}$$

$$SO_3^{2-} \text{(ads)} + [O] \text{ (surface)} \rightarrow SO_4^{2-} \text{ (ads)} \tag{13}$$

$$\Diamond\text{-}HSO_3 + O^{-} \text{ (ads)} \rightarrow \Diamond\text{-}HSO_4^{-} \rightarrow \Diamond\text{-}SO_4^{2-} + H^{+} \tag{14}$$

$$\Diamond\text{-}Fe^{III}OSO_2^{-} \rightarrow \Diamond\text{-}Fe(II) + SO_3^{\cdot-} \text{ (ads)} \tag{15}$$

$$\Diamond\text{-}Fe \text{ (II)} + SO_3^{\cdot-} \text{ (ads)} + [O] \text{ (surface)} \rightarrow \Diamond\text{-}Fe \text{ (III)} + SO_4^{2-} \text{ (ads)} \tag{16}$$

4. Conclusion

In this study, the heterogeneous reactions of SO_2 on α-Fe_2O_3 mixed with three kinds of surfactants were examined under dry and 58% RH conditions to investigate the impact of surfactants on SO_2 uptake and sulfate formation. Results indicated that heterogeneous reactivities of hematite-surfactant mixtures were significantly different due to the presence of different surfactants. Under dry conditions, heterogeneous reactivities decreased with the increase of their concentrations, but the higher reactivities were observed at an appropriate range of CTAB and SDS concentrations when compared to pure hematite, showing that CTAB and SDS at this concentration range can promote SO_2 conversion and sulfate production. Under 58% RH conditions, the heterogeneous reactivities increased first and then decreased with the increasing mass fractions of CTAB and SDS, but pure hematite showed the highest reactivity. While the mixtures containing Triton X-100 had stronger ability to suppress sulfate formation under 58% RH than under dry condition, though these mixtures under 58% RH presented same trend as under dry condition. Within an appropriate mass fraction range of CTAB and SDS, water molecules promote the formation of more and more islands or hemimicelles or admicelles with the increase of the surfactant mass fraction through enhancing surface ionic mobility, which not only renew more and more surface reactive sites but also promote sulfate formation. However, under 58% RH conditions, water molecules promote the adsorption mode transition of Triton X-100 from the adsorption through the terminal OH groups to the adsorption through the ethoxyl groups. This will result in more surface active sites being covered, and consequently lead to a drastically decrease in reactivity and a suppression of SO_2 oxidation.

The results obtained in this study have important implications for understanding the heterogeneous conversion of SO_2 and the formation of sulfate in the atmosphere. Firstly, this experimental study demonstrates the impacts of different surfactants on the heterogeneous oxidation of SO_2 on α-Fe_2O_3, which suggests that the presence of surfactants in aerosols may play significant roles in the heterogeneous oxidation of SO_2 in the atmosphere. Previous field measurement studies have revealed that various surface active species are found to be ubiquitous in tropospheric aerosols. Therefore, this chemistry may inevitably occur on surfaces of airborne dust particles containing surface active species, which would affect the global estimation of the amount of atmospheric sulfate, and further influence the previously estimated radiative forcing and cooling effect of sulfate aerosols in the atmosphere. This impact may be considered in future model simulations. Meanwhile, it is found that surfactants affect the heterogeneous conversion of SO_2 and the formation of sulfate mainly through the occupancies of active sites, the modifications of α-Fe_2O_3 surface properties and the changes of adsorption modes. Therefore, this result may imply that the heterogeneous oxidation of SO_2 in the atmosphere is also impacted through these ways by other surface active species such as long-chain organic acids and diacids and humic like substance (HULIS) (Baduel et al., 2012; Ho et al., 2011; Jimenez et al., 2009), though the cationic, anionic and nonionic surfactants used in this study were from anthropogenic emission sources. Furthermore, it is reasonable to speculate that the presence of surface active species can also influence the heterogeneous reactions of other gaseous inorganic and organic pollutants in the atmosphere such as NO_x and VOCs, and thus affect the

formation of nitrate aerosol and secondary organic aerosols.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.06.050.

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