Chinese Science Bulletin

© 2009 SCIENCE IN CHINA PRESS

Springer

Reaction between sulfur dioxide and iron oxide cationic clusters

YIN Shi[1,2], HE ShengGui[1†] & GE MaoFa[1†]

[1] Beijing National Laboratory for Molecular Sciences (BNLMS), and State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China;
[2] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

The reactivity of sulfur dioxide (SO_2) molecules toward iron oxide cationic clusters ($Fe_mO_n^+$) is studied by a homemade time-of-flight mass spectrometer coupled with a laser ablation/supersonic expansion cluster source and a fast flow reactor. The association products $Fe_mO_nSO_2^+$ can be observed for most of the clusters. The interesting result is that the cooperation effect of SO_2 and water is in favor of the adsorption of gas phase water on specific scale iron oxide clusters ($Fe_2O_2^+$ and $Fe_3O_3^+$). The reactivity information obtained may be useful to investigate atmospheric heterogeneous chemistry of related systems.

time-of-flight mass spectrometer, iron oxide clusters, fast flow reactor, SO_2, reactivity

A great contribution to the troposphere aerosol budget is mineral aerosol[1]. Iron is one of the most important components in mineral aerosol[2]. Iron cycle, in which iron-containing soil dust is transported from land through the atmosphere to the oceans, affects ocean biogeochemistry and hence has feedback effects on climate and dust production[3]. Field measurements of the chemical composition of aerosol particles showed that the major source of iron in dry aerosol appears in the form of highly insoluble iron oxides and oxyhydroxides[1–6]. Sulfur dioxide (SO_2) emits from incomplete combustion of fossil fuel and biomass, whose oxidation leads to acid rain, and its transport is thus a subject of great environmental interest. Researches show that gaseous SO_2 could react directly with mineral aerosol to form particulate sulfate[7,8].

Recently, the heterogeneous reactivity of SO_2 has been observed in metal oxides[9,10], China loess[11], and Saharan mineral[12,13]. Studies of the heterogeneous reactions of SO_2 were undertaken with the recognition that gas-solid reactions could be important in the atmosphere. Currently, a few spectroscopy studies are available to probe the interaction of SO_2 and iron oxides[5,12,14–16]. Equivalent saturation coverages and product ratios of sulfite to sulfate were observed on iron oxide surfaces in the presence of water vapor corresponding to variational relative humidity (RH), suggesting that water had no effect on the adsorption of SO_2[16]. Influence of tropospheric SO_2 emissions on particle formation and the stratospheric humidity have been studied and the conclusion implies that SO_2 emissions have been suggested to contribute to the increase of stratospheric water vapor levels and the amount of water that entered the stratosphere in the condensed phase[17].

In describing and accounting for phenomena in atmospheric science, clusters have played a role[18] and gas phase metal oxide clusters composed of limited number of atoms that are fully accessible by both experiment and theory are excellent model systems to investigate for understanding the intrinsic reaction mecha-

---

Received January 7, 2009; accepted February 18, 2009
doi: 10.1007/s11434-009-0527-2

† Corresponding authors (email: shengguihe@iccas.ac.cn; gemaofa@iccas.ac.cn)

Supported by the Knowledge Innovation Program of the Chinese Academy of Sciences(Grant Nos. KJCX2-YW-N24, KZCX2-YW-205), the Major State Basic Research Development Program of China and Technology of China(Grant No. 2006CB-403701), and the National Natural Science Foundation of China (Grant Nos. 40830101, 20673123).

Citation: Yin S, He S G, Ge M F. Reaction between sulfur dioxide and iron oxide cationic clusters. Chinese Sci Bull, 2009, 54: 4017—4020, doi: 10.1007/s11434-009-0527-2

nisms in the condensed phase reactive processes[19,20].

Low-temperature oxidation of carbon-cluster anions which serve as models for the local structural features of active soot particle sites for black-carbon soot by SO_2 has been studied[21]. The chemistry of gas phase iron oxide clusters has been investigated experimentally[22–30]. However, there is no report on the reactivity of the $Fe_mO_n^+$ toward SO_2, which is a topic of the current study. Based on our previous investigation on the formation, distribution, and structures of iron oxide cationic clusters by using a built fast flow reactor[31], we experimentally studied the reactivity of $Fe_mO_n^+$ toward SO_2 under gas phase conditions. In the fast flow reactor, the preformed clusters react with reactant seeded in inert carrier gas (Ar). The gas phase reaction and detection (through mass spectrometry) ensure that the reaction conditions are well defined and controlled in an easy and reproducible way without sever interference of surface inhomogeneous, solvent effects, impurities, temperature gradients, etc. The aim of this study is to explore the reaction property of SO_2 molecules toward iron oxide cationic clusters with the experimental methods. The reactivity information obtained in this work may be considered to interpret surface chemistry of related systems.

The experiments performed in this study are conducted with a time-of-flight mass spectrometer (TOF-MS) coupled with a laser ablation/supersonic expansion cluster source and a fast flow reactor, which were described previously[31,32]. The vacuum system of the apparatus consists of two chambers. One of the chambers is used for cluster generation/reaction and the other is for cluster ion detection. The two chambers are connected through a 5 mm diameter skimmer. The iron oxide clusters are generated by the reaction of laser ablation-generated iron plasmas with O_2 seeded (0.5%) in the helium carrier gas. As trace water and O_2 seeded in the helium carrier gas, the water-association iron oxide clusters were generated simultaneously. The typical backing pressure of the He gas is 5 atm. To generate the iron plasmas, an Nd:YAG laser beam (532 nm, 5 mJ/pulse, 8 ns duration, 10 Hz) is focused onto an iron metal disk (15 mm diameter, 0.13 mm thickness, 99.7% purity from Aldrich). The disk is rotated and translated to continually expose a fresh surface. The carrier gas seeded with O_2 is controlled by the first pulsed valve (General Valve, series 9). The clusters are formed in a narrow cluster formation channel (2 mm inner diameter (i.d.)) that contains a waiting room (3 mm i.d.). The lengths of the channel and the waiting room are adjustable to optimize the cluster growth conditions. Increase of the waiting room length is conducive to the formation of smaller clusters. The typical lengths used are 1 cm for the waiting room and 2 cm for the rest of the channels. A fast flow reactor with 6 mm i.d. and 8 cm length is coupled with the narrow cluster formation channel. The generated iron oxide cluster cations react with reactant molecules (SO_2) seeded in argon carrier gas controlled by the second pulsed valve. The amount of gas pulsed into the chamber by the first value is about 80 times the gas pulsed by the second valve. Durations of the two gas pulses are about the same (~250 μs) in this study. The instantaneous gas pressure in the fast flow reactor is about 8 Torr. The temperature is close to ambient temperature due to a large number of collisions between cluster and carrier gas in the reactor[33]. The ionic species in the beam of the reactants, the products, and the buffer gases were detected by the TOF-MS equipped with pulsed power supplies.

The mass spectra for the reactions of $Fe_mO_n^+$ clusters with 1% SO_2 seeded in the argon are plotted in Figures 1 and 2 for $Fe_{1,2}O_n^+$ and $Fe_{3,4}O_n^+$, respectively. Reference spectra for cluster collision with pure argon are also provided for comparison. Figures 1 and 2 show that iron oxide clusters (denoted as "Ar") are generated for $FeO_{2,4}^+$, $Fe_2O_{2–6}^+$, $Fe_3O_{3–7}^+$, $Fe_4O_{5–7}^+$, $Fe_5O_{7,8}^+$, etc. as reported by us previously, and a few hydrogen impurity peaks can be assigned as iron oxide clusters with one or more H_2O molecules $Fe_mO_n(H_2O)_y^+$[31]. In the experiments, different concentrations (0–10%) of O_2 were

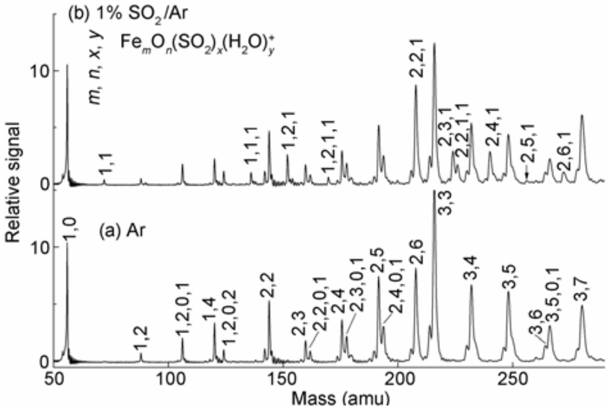

Figure 1 TOF spectra for reaction of $Fe_mO_n^+$ (m = 1 and 2) with 1% SO_2 seeded in argon. Symbols m, n, x, y denote mass spectrometer-detected species $Fe_mO_n(SO_2)_x(H_2O)_y^+$. The downward arrows in the top panel indicate that at the mass positions of $Fe_2O_5SO_2^+$, the products are not observed (or barely observed due to the experimental uncertainty).

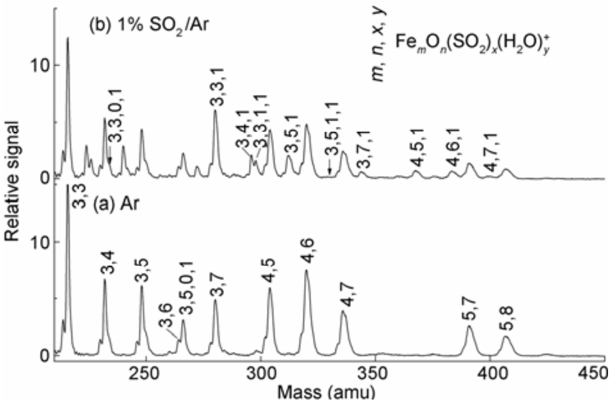

Figure 2 TOF spectra for reaction of $Fe_mO_n^+$ (m = 3 and 4) with 1% SO_2 seeded in argon. See caption of Figure 1 for the label explanation.

tested for generating the iron oxide cationic clusters. In this work, a typical mass distribution which covers small clusters generated with 0.5% O_2 is presented.

After reacting with 1% SO_2, the mass signals of $FeO_{2,5}^+$, $Fe_2O_{2-5}^+$, $Fe_3O_{3-5}^+$ and $Fe_4O_{5-7}^+$ decrease (top panels of Figures 1 and 2), and the association products ($FeO_{1,2}SO_2^+$, $Fe_2O_{3,4,6}SO_2^+$, $Fe_3O_{4,5,7}SO_2^+$, $Fe_4O_{5-7}SO_2^+$) are observed. As association products $Fe_2O_6SO_2^+$ and $Fe_3O_7SO_2^+$, are observed, the depletions of the corresponding pre-formed $Fe_2O_6^+$, and $Fe_3O_7^+$ clusters should be observed. But as shown in Figures 1 and 2, the signals of mass peaks at 208 amu ($Fe_2O_6^+$) and 280 amu ($Fe_3O_7^+$) positions increase, implying that some new products may enhance the intensity of signals at the mass position of $Fe_2O_6^+$ and $Fe_3O_7^+$. And the decrease of mass signals of $Fe_2O_2^+$ and $Fe_3O_3^+$ is observed, so the increase of mass signals 208 amu and 280 amu is because the association products $Fe_2O_2SO_2^+$ (208 amu) and $Fe_3O_3SO_2^+$ (280 amu) are produced.

Although FeO_4^+ and $Fe_2O_5^+$ are quite reactive toward SO_2, the corresponding association products $FeO_4SO_2^+$ and $Fe_2O_5SO_2^+$ are not observed. The observed products ($FeO_2SO_2^+$ and $Fe_2O_{2-6}SO_2^+$) that can be produced from reactions of $FeO_{2,4}^+$ and $Fe_2O_{2-6}^+$ with SO_2, $FeO_2SO_2^+$ and $Fe_2O_3SO_2^+$ have strong signals and their signals magnitudes are significantly greater than the decrease signals of FeO_2^+ and $Fe_2O_3^+$. The conclusion is that the reaction of FeO_4^+ and $Fe_2O_5^+$ with SO_2 produces $FeO_2SO_2^+$ and $Fe_2O_3SO_2^+$. Similar to the reaction of FeO_4^+ and $Fe_2O_5^+$ with CO which produced FeO_2CO^+ and $Fe_2O_3CO^+$[30], the mechanism may be interpreted by simple substitution reactions: $Fe_2O_5^+ + SO_2 \rightarrow Fe_2O_3SO_2^+ + O_2$ and $FeO_4^+ + SO_2 \rightarrow FeO_2SO_2^+ + O_2$. So it can be generally concluded that SO_2 is easy to be absorbed on small cationic iron oxide clusters ($Fe_{1-4}O_n^+$) and larger clusters (such as $Fe_{3,4}O_n^+$ versus $Fe_{1,2}O_n^+$) may be less reactive than the smaller ones for the result, in which the signals of association products are gradually weakened with the corresponding preformed $Fe_mO_n^+$ clusters growth as shown in Figures 1 and 2.

The interesting finding is that some water-association products ($FeO_2SO_2H_2O^+$, $Fe_2O_2SO_2H_2O^+$ and $Fe_3O_3SO_2H_2O^+$) are also observed. As shown in Figures 1 and 2, the mass signals of $Fe_2O_2SO_2H_2O^+$ and $Fe_3O_3SO_2H_2O^+$ are strong, but the magnitudes of the signals of the corresponding reactant ions ($Fe_2O_2H_2O^+$ and $Fe_3O_3H_2O^+$) are little reduced. It documents that these water-association products may not be produced by adsorption of one sulfur dioxide molecule on $Fe_2O_2H_2O^+$ and $Fe_3O_3H_2O^+$ reactant ions. This supposition is also supported by the observation that $Fe_3O_5SO_2H_2O^+$ is not observed, although the reactant ion $Fe_3O_5H_2O^+$ is abundant. So the reactivity of $Fe_mO_n^+$ toward SO_2 is usually higher than that of water containing clusters, but the $Fe_mO_n^+$ associated with SO_2 is easier to adsorb water molecule. The products $Fe_2O_2SO_2H_2O^+$ and $Fe_3O_3SO_2H_2O^+$ may be produced from the further reaction of sulfur dioxide association products ($Fe_2O_2SO_2^+$ and $Fe_3O_3SO_2^+$) with the trace water in the gas phase. The result may imply that the cooperation effect of sulfur dioxide and water on specific scale iron oxide clusters ($Fe_2O_2^+$ and $Fe_3O_3^+$) is in favor of the adsorption of gas phase water.

In conclusion, the time-of-flight mass spectrometry is adopted to study the reactivity of SO_2 toward $Fe_mO_n^+$ under gas phase, under near room temperature conditions. The association reaction products $FeO_{1,2}SO_2^+$, $Fe_2O_{2-4,6}SO_2^+$, $Fe_3O_{3-5,7}SO_2^+$, and $Fe_4O_{5-7}^+SO_2$ are observed, implying that $Fe_mO_nSO_2^+$ can be observed for most of the clusters. As the signals of association products gradually are weakened with the corresponding preformed $Fe_mO_n^+$ clusters growth, larger $Fe_mO_n^+$ clusters are generally found to be less reactive than the smaller ones in the experiments. The reactivity of $Fe_mO_n^+$ toward SO_2 is usually higher than that of water containing clusters, but the $Fe_mO_n^+$ associated with SO_2 may be easier to adsorb water molecule. Some water association products are produced from the further reaction of sulfur dioxide association products ($Fe_2O_2SO_2^+$ and $Fe_3O_3SO_2^+$) with the trace water in the gas phase. So the cooperation effect of sulfur dioxide

Yin S et al. Chinese Science Bulletin | November 2009 | vol. 54 | no. 21 **4019**

and water is in favor of the adsorption of gas phase water on specific scale iron oxide clusters ($Fe_2O_2^+$ and $Fe_3O_3^+$). Iron oxide cationic clusters serve as models for the local structural features of active iron oxide particle sites for iron oxide mineral aerosol. The reactivity information obtained in our work can be used to investigate atmospheric heterogeneous chemistry of related systems.

1 Deguillaume L, Leriche M, Desboeufs K, et al. Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters. Chem Rev, 2005, 105: 3388—3431[DOI]

2 Jambor J L, Dutrizac J E. Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. Chem Rev, 1998, 98: 2549—2586[DOI]

3 Jickells T D, An Z S, Andersen K K, et al. Global iron connections between desert dust, ocean biogeochemistry, and climate. Science, 2005, 308: 67—71[DOI]

4 Leland J K, Bard A J. Photochemistry of colloidal semiconducting iron oxide polymorphs. J Phys Chem, 1987, 91: 5076—5083[DOI]

5 Weckler B, Lutz H D. Lattice vibration spectra. Part XCV. Infrared spectroscopic studies on the iron oxide hydroxides goethite (α), akaganéite (β), lepidocrocite (γ), and feroxyhite (δ). Eur J Solid State Inorg Chem, 1998, 35: 531—544[DOI]

6 Hoffmann P, Dedik A N, Ensling J, et al. Speciation of iron in atmospheric aerosol samples. J Aerosol Sci, 1996, 27: 325—337[DOI]

7 Adams J W, Rodriguez D, Cox R A. The uptake of SO_2 on Saharan dust: A flow tube study. Atmos Chem Phys, 2005, 5: 2679—2689

8 Zhuang G S, Yi Z, Duce R A, et al. Link between iron and sulfur cycles suggested by detection of iron (II) in remote marine aerosols. Nature, 1992, 355: 537—539[DOI]

9 Goodman A L, Li P, Usher C R, et al. Heterogeneous uptake of sulfur dioxide on aluminum and magnesium oxide particles. J Phys Chem A, 2001, 105: 6109—6120[DOI]

10 Usher C R, Al-Hosney H, Carlos-Cuellar S, et al. A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles. J Geophys Res, 2002, 107: 4713

11 Ullerstam M, Vogt R, Langer S, et al. The kinetics and mechanism of SO_2 oxidation by O_3 on mineral dust. Phys Chem Chem Phys, 2002, 4: 4694—4699[DOI]

12 Ullerstam M, Johnson M S, Vogt R, et al. Drifts and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust. Atmos Chem Phys, 2003, 3: 2043—2051

13 Faust B C, Hoffmann M R. Photoinduced reductive dissolution of α-Fe_2O_3 by Bisulfite. Environ Sci Technol, 1986, 20: 943—948[DOI]

14 Toledano D S, Henrich V E. Kinetics of SO_2 adsorption on photoexcited α-Fe_2O_3. J Phys Chem B, 2001, 105: 3872—3877[DOI]

15 Fu H, Wang X, Wu H, et al. Heterogeneous uptake and oxidation of SO_2 on iron oxides. J Phys Chem C, 2007, 111: 6077—6085[DOI]

16 Baltrusaitis J, Cwiertny D M, Grassian V H. Adsorption of sulfur dioxide on hematite and goethite particle surfaces. Phys Chem Chem Phys, 2007, 9: 5542—5554[DOI]

17 Notholt J, Luo B P, Fueglistaler S, et al. Influence of tropospheric SO_2 emissions on particle formation and the stratospheric humidity. Geophys Res Lett, 2005, 32: L07810[DOI]

18 Castleman Jr A W, Jena P. Clusters: A bridge across the disciplines of environment, materials science, and biology. Proc Natl Acad Sci USA, 2006, 103: 10554—10559[DOI]

19 Muetterties E L. Molecular metal clusters. Science, 1977, 196: 839—848[DOI]

20 Jena P, Castleman Jr A W. Clusters: A bridge across the disciplines of physics and chemistry. Proc Natl Acad Sci USA, 2006, 103: 10560—10569[DOI]

21 Leavitt A J, Wyrwas R B, Wallace W T, et al. Efficient low-temperature oxidation of carbon-cluster anions by SO_2. J Phys Chem A, 2005, 109: 6218—6222[DOI]

22 Sakurai M,Watanabe K, Sumiyama K, et al. Magic numbers in Fe clusters produced by laser vaporization source. J Phys Soc Jpn, 1998, 67: 2571—2573[DOI]

23 Wang Q, Sun Q, Sakurai M, et al. Geometry and electronic structure of magic iron oxide clusters. Phys Rev B, 1999 59: 12672—12677[DOI]

24 Sun Q, Sakurai M, Wang Q, et al. Geometry and electronic structures of magic transition-metal oxide clusters M_9O_6 (M = Fe, Co, and Ni). Phys Rev B, 2000, 62: 8500—8507[DOI]

25 Sakurai M, Watanabe K, Sumiyama K, et al. Magic numbers in transition metal (Fe, Ti, Zr, Nb, and Ta) clusters observed by time-of-flight mass spectrometry. J Chem Phys, 1999, 111: 235—238[DOI]

26 Shin D N, Matsuda Y, Bernstein E R. On the iron oxide neutral cluster distribution in the gas phase. I. Detection through 193 nm multiphoton ionization. J Chem Phys, 2004, 120: 4150—4156[DOI]

27 Shin D N, Matsuda Y, Bernstein E R. On the iron oxide neutral cluster distribution in the gas phase. II. Detection through 118 nm single photon ionization. J Chem Phys, 2004, 120: 4157—4164[DOI]

28 Reilly N M, Reveles J U, Johnson G E, et al. Influence of charge state on the reaction of $FeO_3^{+/-}$ with carbon monoxide. Chem Phys Lett, 2007, 435: 295—300[DOI]

29 Reilly N M, Reveles J U, Johnson G E, et al. Experimental and theoretical study of the structure and reactivity of $Fe_{1\text{-}2}O_{\leqslant 6}^-$ clusters with CO. J Phys Chem A, 2007, 111: 4158—4166[DOI]

30 Reilly N M, Reveles J U, Johnson G E, et al. Experimental and theoretical study of the structure and reactivity of $Fe_mO_n^+$ (m = 1, 2; n = 1−5) with CO. J Phys Chem C, 2007, 111: 19086—19097[DOI]

31 Yin S, Xue W, Ding X L, et al. Formation, distribution, and structures of oxygen-rich iron and cobalt oxide clusters. Inter J Mass Spectros, 2009, 281: 72—78[DOI]

32 Yin S, Ma Y, Du L, et al. Experimental and theoretical studies of the reaction between cationic vanadium oxide clusters and acetylene. Chinese Sci Bull, 2008, 53: 3829—3839[DOI]

33 Geusic M E, Morse M D, O'Brien S C. Surface reactions of metal clusters I: The fast flow cluster reactor. Rev Sci Instrum, 1985 56: 2123—2130[DOI]