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# Atmospheric heterogeneous reaction of acetone: Adsorption and desorption kinetics and mechanisms on SiO<sub>2</sub> particles

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Acetone plays an important role in photooxidation processes in the atmosphere. Up to date, little is known regarding the heterogeneous fate of acetone. In this study, the adsorption and desorption processes of acetone on SiO<sub>2</sub> particles, which are the major constituent of mineral dust in the atmosphere, have been investigated for the first time under the simulated atmospheric conditions, using *in situ* transmission Fourier transform infrared spectroscopy. It is found that acetone molecules are adsorbed on the surfaces of SiO<sub>2</sub> particles by van der Waals forces and hydrogen bonding forces in a nonreactive and reversible state. The rates of initial adsorption and initial desorption, initial uptake coefficients and adsorption concentrations at equilibrium have been determined at different relative humidity. The presence of water vapor cannot result in the formation of new substances, but can decrease the adsorption ability by consuming or overlapping the isolated OH groups on the surfaces of SiO<sub>2</sub> particles. In the desorption process, a considerable amount of acetone molecules will remain on SiO<sub>2</sub> particles in dry air, whereas acetone molecules are almost completely desorbed at a high relative humidity. In order to evaluate the role of heterogeneous reactions of acetone and other carbonyl compounds in the atmosphere, a new model fitting the atmospheric conditions is needed.

carbonyl compound, mineral dust, heterogeneous reaction, troposphere

Carbonyl compounds, mostly produced by the photooxidation of volatile organic compounds (VOCs), play an important role in the photochemical oxidant cycle<sup>[1]</sup>. On the global scale, acetone is one of the most dominant carbonyls in the middle to upper troposphere, and its photolysis represents a significant source of peroxyacetyl nitrates (PAN) and  $HO_x$  (OH and  $HO_2$ ) radicals<sup>[2]</sup>. Model calculations suggest that in the upper troposphere the loss of acetone by photolysis provides a  $HO_x$  source which is 5 times greater than that exploited by the  $O(^1D)+H_2O$  reactions<sup>[3,4]</sup>.

However, little is known regarding the heterogeneous chemistry of acetone on aerosol surfaces or its overall significance. Laboratory studies to quantify what reactions take place on aerosol surfaces and how these reactions affect the photochemical oxidant cycle are needed to address this issue. There have been some laboratory studies on heterogeneous chemistry of acetone on some oxide constitutes of mineral dust in the atmosphere; for example, Li et al. have determined the initial uptake coefficients of acetone on SiO<sub>2</sub>, α-Al<sub>2</sub>O<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub> with a Knudsen cell, in which experiments were operated in the absence of air and water vapor under low pressure. However, few of these laboratory studies were carried out under real atmospheric conditions. In addition, the acetone formed or adsorbed on mineral dust may escape into the gas phase from the particles, thus

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the desorption kinetics of acetone on mineral dust should also be taken into account. Considering the importance of acetone in the atmosphere and the limitation of previous studies, it is crucial to further study its heterogeneous reactions.

As a first step to understand the heterogeneous reactions of acetone in the atmosphere, this paper has presented an experimental study on the adsorption and desorption kinetics of acetone on SiO<sub>2</sub> particles under the simulated atmospheric conditions. As the major constituent of mineral dust in the atmosphere, SiO<sub>2</sub> has an abundance of approximately 60% by weight [6,7]. Thus SiO<sub>2</sub> was used as a model for mineral dust in the atmosphere in this study. The technique of transmission Fourier transform infrared (T-FTIR) spectrometry was employed for the in situ investigation to understand the detailed physical chemistry occurring on the surfaces of SiO<sub>2</sub> particles at 295K, and in 1atm dry and humid air. Both the kinetics and mechanisms of adsorption and desorption of acetone on SiO<sub>2</sub> are discussed within the context.

## 1 Experiment section

In the laboratory study for atmospheric heterogeneous reactions, the advantage of FTIR spectrometry is that it can be used to investigate reactants and products without interrupting the reaction processes<sup>[8–11]</sup>. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique and transmission FTIR (T-FTIR) technique are two kinds of applied methods, and generally the latter has better repeatability and its quantification is more accurate. In the present study, T-FTIR was used to probe the heterogeneous reaction of acetone.

#### 1.1 Reagents

The SiO<sub>2</sub> (Zhoushan Nanometer Materials Inc, 99.9+%) powder with a Brunauer-Emmett-Teller (BET) surface area measured as 640 m<sup>2</sup>/g was used. The mean particle diameter of the powder is around 40 nm, determined by transmission electron microscopy. The vapor of acetone was generated from its liquid sample (Fluka, >99.7%). N<sub>2</sub> (>99.999%, Beijing Pryx Applied Gas Company Limited) and O<sub>2</sub> (>99.995%, Beijing Analytical Instrument Factory) gases were used. All solutions were prepared with Milli-Q water.

#### 1.2 Experimental apparatus

The experiments were carried out in a reactor which

consists of a quartz cell with two infrared windows made of ZnSe (Infrared Analysis Corp., California, USA). The volume of the reactor is ~90 mL, with an optical path of 15 cm. The Reynolds number was calculated to be 63 (<4000), indicating that the air in the reactor is in the condition of laminar current. SiO<sub>2</sub> powder was evenly coated on a 250-mesh stainless steel grid and then the grid was mounted inside the reactor. The FTIR spectrometer (Nicolet Nexus, USA) equipped with a mercury cadmium telluride (MCT) detector was used to *in situ* monitor reaction processes and record T-FTIR spectra. The infrared beam was introduced to pass through the SiO<sub>2</sub> powder coated on the grid. All spectra were recorded at a resolution of 4 cm<sup>-1</sup>, and 64 scans were usually averaged for each spectrum.

Acetone was analyzed by detecting its derivative of 2,4-dinitrophenyhydrazine (DNPH) with high performance liquid chromatography (HPLC) (Agilent 1100, USA) equipped with a ultraviolet detector. A detection wavelength of 360 nm was used and the sampling volume was 20  $\mu$ L. The eluting solution was composed of 45% water and 55% acetonitrile, with a total flow rate of 1.2 mL  $\cdot$  min<sup>-1</sup>.

#### 1.3 Experimental process

For each experiment, SiO<sub>2</sub> powder with about 5 mg weight was used. The reactor with SiO<sub>2</sub> powder was evacuated at room temperature for at least 1h prior to the introduction of synthetic dry or humid air, in order to remove most of the adsorbed ambient air.

The vapor of acetone was generated from its liquid sample at certain temperature and pressure by a diffusion tube<sup>[12]</sup>. The acetone gaseous flow was diluted by synthetic air (mixture of N<sub>2</sub> and O<sub>2</sub> in a volume ratio of 4:1), and then mixed with another synthetic air flow containing water vapor obtained by a water vapor generator. The combined flow was introduced into the reactor, at a total rate of 400 standard cubic centimeters per minute (sccm). The concentration of the acetone gas passing through the reactor was  $4.7 \times 10^{15}$  molecule cm<sup>-3</sup>, which was determined by T-FTIR and HPLC.

In all experiments, the synthetic air at required relative humidity (RH) was continuously introduced into the reactor until SiO<sub>2</sub> particles achieved adsorption equilibrium. The acetone-unexposed sample was used to collect a background spectrum. Then the valve was altered so that the acetone gas in the synthetic air at the same relative humidity was constantly introduced into the reactor.

The T-FTIR spectra were *in situ* recorded. After the adsorption of acetone on SiO<sub>2</sub> particles was saturated and the saturation lasted for 30 min, SiO<sub>2</sub> particles were quickly taken out and immersed in DNPH solution to derivatize acetone. The solution sample was kept for about 12 h in dark at room temperature, and then determined with HPLC. During the desorption experiments, after the adsorption of acetone on SiO<sub>2</sub> particles was saturated, the acetone-free synthetic air at required relative humidity was introduced into the reactor, and then the T-FTIR spectra were *in situ* recorded. The total gas flow rate in the reactor in all the experiments mentioned above was 400 sccm and the reaction was controlled at temperature of 295±2 K and 1atm pressure.

## 2 Results and discussion

## 2.1 Spectra of reaction processes

The adsorption and desorption processes of acetone on SiO<sub>2</sub> particles in dry air were investigated, and the T-FTIR spectra of these processes are shown in Figure 1.

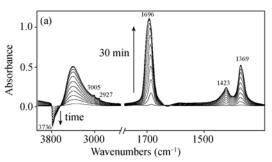
Figure 1(a) shows a time series of spectra of acetone adsorbed on SiO<sub>2</sub> particles. The most intensive band at 1696 cm<sup>-1</sup> is assigned to the stretching motion of carbonyl group (C=O). The asymmetric and symmetric stretching vibrations of the C-H band in methyl groups appear at 3005 cm<sup>-1</sup> and 2927 cm<sup>-1</sup> (very weak), respectively. The absorption bands at 1423 cm<sup>-1</sup> and 1369 cm<sup>-1</sup> are assigned to the asymmetric and symmetric deformation vibrations of C-H respectively. All of those bands mentioned above increased with the increasing adsorption time, suggesting that acetone molecules continuously accumulate on the surface of SiO<sub>2</sub> particles. And the frequencies of these absorption bands for acetone molecules adsorbed on SiO2 are very close to those of acetone in the gas phase, suggesting that no new substances were formed on SiO2 surface. The decrease in intensity of the band at 3736cm<sup>-1</sup>, associated with the isolated OH group, and a concomitant growth of the band at 3000—3600 cm<sup>-1</sup>, suggests that a hydrogen-bonding interaction between the carbonyl groups and the surface hydroxyl groups occurred. A similar phenomenon of other carbonyls such as formaldehyde adsorbed on SiO<sub>2</sub> was observed in previous studies<sup>[13–16]</sup>.

The desorption occurred when the acetone-free air was introduced into the reactor after the adsorption of acetone on SiO<sub>2</sub> achieved equilibrium, as shown in Figure 1(b). The intensity of the band at 3736 cm<sup>-1</sup> increased with the increasing desorption time, meanwhile, the band at 3000—3600 cm<sup>-1</sup> decreased, suggesting that the hydrogen-bondings were broken and the isolated OH groups were recovered on the SiO<sub>2</sub> surface. Therefore, it can be concluded that the acetone molecules are weakly and reversibly absorbed on the surface of SiO<sub>2</sub> particles.

## 2.2 Kinetics of adsorption and desorption

Figure 2 illustrates a time series of concentration of acetone adsorbed on SiO<sub>2</sub> particles sequentially exposed to the acetone-contained dry air and acetone-free dry air. It is found that the adsorption proceeds via three stages during the investigation period. In the initial stage, acetone molecules are rapidly adsorbed and the concentration of acetone absorbed on SiO2 increases at a stable rate. The second is the transition stage in which the concentration of acetone adsorbed increased slowly and the rate of adsorption decreased gradually, suggesting a significant decrease of surface sites. The third is an equilibrium stage. The adsorption of acetone on the surface was saturated; hence the adsorption arrived at an equilibrium. According to the fitted line in the initial stage, the rate of initial adsorption is obtained as (1.0± 0.1)× $10^{15}$  molecules m<sup>-2</sup>·s<sup>-1</sup> based the BET area.

It is found that the rate of desorption deceases gradu-



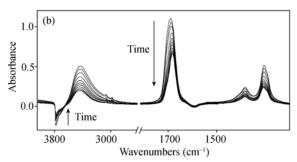


Figure 1 T-FTIR spectra of heterogeneous reactions of acetone on SiO<sub>2</sub> particles in 1 atm dry air. (a) Adsorption process; (b) desorption process. The acetone-unexposed sample was used as a background spectrum.

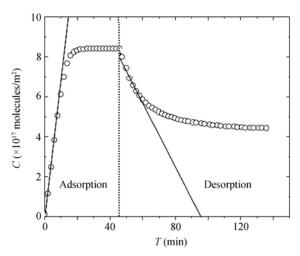


Figure 2 Kinetics curves of adsorption and desorption of acetone on  $SiO_2$  particles in 1 atm dry air.

ally with the decreasing reaction time in the desorption process, as shown in Figure 2. From the fitted line in the initial stage of desorption, the rate of initial desorption is obtained as  $(3.2\pm0.1)\times10^{14}$  molecules m<sup>-2</sup> s<sup>-1</sup>, which is one third of the adsorption rate. Noticeably, only about half amount of the acetone molecules on SiO2 particles was desorbed into the gas phase, though the desorption proceeded for a long time in dry air. After this process proceeded for 2 h, the rate of desorption approached zero. Carlos-Cuellar et al. [15] reported that some carbonyls would completely escape from the particle surface upon evacuation of the gas phase, but they have not studied the issue at a normal pressure of air. As a result of the present study, it is found, under the atmospheric conditions, that half of acetone molecules adsorbed may stay on the surfaces of SiO<sub>2</sub> particles for more than several hours.

The uptake coefficient,  $\gamma$ , is simply a measure upon how likely the gas molecule will be taken up by the surface of particles, through either adsorption or reaction, per a gas-phase collision basis<sup>[17]</sup>. The uptake coefficient  $\gamma$  can be determined by the following equations<sup>[18]</sup>:

$$\gamma = \frac{d\{ra\}/dt}{Z},\tag{1}$$

$$Z = \frac{1}{4}\overline{c}A_{\rm s}[ra],\tag{2}$$

$$\overline{c} = \sqrt{\frac{8RT}{\pi M_{ra}}},\tag{3}$$

where Z is the rate of collisions between gaseous reactant molecules and  $SiO_2$  surface,  $\overline{c}$  the mean molecular velocity of the gaseous reactant molecules,  $A_s$  the

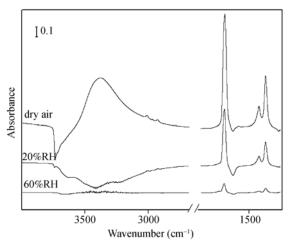
effective sample surface area, R the gas constant, T the temperature and  $M_{ra}$  the molecular weight of reactant. Concentrations-marked  $\{ra\}$  indicates the concentration of reactant on the surfaces of particles, whereas [ra] indicates the concentration of reactant in the gas phase. In this study, acetone molecules flow through the particles coated on the stainless grid, thus they have enough opportunities to contact and react with  $SiO_2$  particles. Hence the BET surface area is adopted as the effective sample surface area. As a result, the initial uptake coefficient,  $\gamma_0$ , for acetone uptaken by  $SiO_2$  particles in dry air was obtained as  $(2.4\pm0.3)\times10^{-9}$ .

Li et al. [5] determined the  $\gamma_0$  for acetone on SiO<sub>2</sub> as  $6.2 \times 10^{-6}$  by a Knudsen cell based on the BET area. Their value is three orders of magnitude greater than the value determined in our study. It should be pointed that such a large gap between these two values mainly results from the adopted determining methods. The Knudsen cell is a low-pressure flow reactor in which there are only acetone molecules exposed to the 'clear' surfaces of particles. Unlike the Knudsen cell, the flow tube reactor used in this study runs under the condition of a normal pressure of air, thus carbonyl molecules would significantly compete with N<sub>2</sub> and O<sub>2</sub> molecules in the gas-phase and on the surfaces of particles, resulting in much fewer surface sites for absorbing acetone. Therefore, the  $y_0$  value determined by the reactor in this study should be much lower than that determined by a Knudsen cell. However, the condition in this study approaches that in the troposphere.

## 2.3 Effect of relative humidity

The effect of water vapor on the heterogeneous reactions needs to be considered. Thus a further investigation for adsorption and desorption processes of acetone on SiO<sub>2</sub> particles in humid air was carried out. Figure 3 shows a comparison of T-FTIR spectra at adsorption equilibrium in dry and humid air. It is found that the frequencies and shapes of absorption bands in infrared spectra for acetone adsorbed on SiO<sub>2</sub> are quite similar at different relative humidity, suggesting that the presence of water vapor can not result in the formation of new substances.

However, the intensity of absorbance band at 1696 cm<sup>-1</sup>, which is assigned to carbonyl groups, decreases when the relative humidity increases, suggesting that the equilibrium adsorption amount of acetone molecules may decrease with the increase of relative humidity. This was further proved by the analysis of HPLC, as



**Figure 3** T-FTIR spectra of equilibrium adsorption of acetone on SiO<sub>2</sub> particles in dry and humid air. The acetone-unexposed samples were used to collect background spectra at required relative humidity.

shown in Table 1. In order to confirm the accuracy for quantifying acetone adsorbed with the technique of T-FTIR in the presence of water vapor, the ratio, f, of the concentration of acetone versus the integrated absorbance (int.abs) of carbonyl groups peaked at 1696 cm<sup>-1</sup> was determined under dry and humid conditions. The f values are obtained in the relative humidity region of 0-80%, as shown in Table 1. It can be seen that the relative error is less than 20%. This means that it is feasible to quantify acetone adsorbed with T-FTIR in this relative humidity region.

The desorption processes at different relative humidity are illustrated in Figure 4. The amount of acetone

molecules remaining on the surfaces of SiO<sub>2</sub> particles after the desorption proceeded for 2 h was also determined at different relative humidity as listed in Table 1. It can be seen that this amount negatively correlated with the relative humidity. Moreover, acetone molecules adsorbed almost completely escape from the SiO<sub>2</sub> particles at 60% relative humidity.

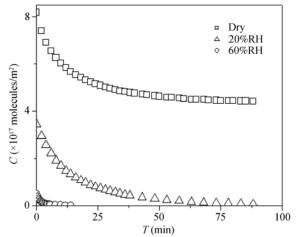


Figure 4 Desorption curves of acetone on SiO<sub>2</sub> particles in dry and humid air.

The kinetics curves of adsorption and desorption of acetone on SiO<sub>2</sub> particle surface were determined at different relative humidity. The initial rates and initial uptake coefficients are listed in Table 2. It can be seen that both the rate of initial adsorption and the rate of initial desorption decrease slightly with the increase of relative humidity. It is also found that the rate of initial adsorp-

Table 1 Concentrations of acetone on SiO<sub>2</sub> particles, and ratios (f) of the concentration of acetone adsorbed versus the integrated absorbance

RH -	Concentration of acetone on SiO <sub>2</sub> (molecules m <sup>-2</sup> )		f (molecule m <sup>-2</sup> int.abs <sup>-1</sup> )
	adsorption at equilibrium a)	remains after desorption b)	f (molecule iii liit.abs )
0% (dry)	(8.4±0.1)×10 <sup>17</sup>	$(4.4\pm0.2)\times10^{17}$	(2.7±0.1)×10 <sup>16</sup>
20%	$(4.0\pm0.1)\times10^{17}$	$(4.0\pm0.5)\times10^{15}$	$(2.6\pm0.2)\times10^{16}$
40%	$(1.3\pm0.1)\times10^{17}$	$(8.6\pm1.5)\times10^{14}$	$(2.5\pm0.1)\times10^{16}$
60%	$(5.3\pm0.3)\times10^{16}$	$<6.2\times10^{14}$	$(2.2\pm0.4)\times10^{16}$
80%	$(4.3\pm0.7)\times10^{16}$	<5.4×10 <sup>14</sup>	$(2.3\pm0.4)\times10^{16}$

a) The concentrations of acetone on SiO<sub>2</sub> particles at adsorption equilibrium; b) the concentrations of acetone remaining on SiO<sub>2</sub> particles after the desorption proceeded for 2 h.

Table 2 Rates of initial adsorption and initial desorption and coefficients of initial uptake for acetone on SiO<sub>2</sub> particles

RH	Initial adsorption rate (molecules m <sup>-2</sup> s <sup>-1</sup> )	Initial desorption rate (molecules m <sup>-2</sup> s <sup>-1</sup> )	γο <sup>a)</sup>
0%(dry)	(1.0±0.1)×10 <sup>15</sup>	(3.2±0.1)×10 <sup>14</sup>	(2.4±0.3)×10 <sup>-9</sup>
20%	$(6.2\pm0.1)\times10^{14}$	$(2.6\pm0.1)\times10^{14}$	$(1.5\pm0.2)\times10^{-9}$
40%	$(5.7\pm0.3)\times10^{14}$	$(2.6\pm0.1)\times10^{14}$	$(1.3\pm0.3)\times10^{-9}$
60%	$(3.7\pm0.4)\times10^{14}$	$(1.9\pm0.1)\times10^{14}$	$(9.0\pm0.4)\times10^{-10}$
80%	$(3.6\pm0.2)\times10^{14}$	$(2.1\pm0.5)\times10^{14}$	$(8.6\pm0.2)\times10^{-10}$

a) All the  $\gamma_0$  values were calculated with the same BET area based on the unhydrated surface.

tion is larger than the rate of initial desorption at the same relative humidity, suggesting that acetone is inclined to stay on the surfaces of SiO<sub>2</sub> particles.

From Table 2, it can be seen that the coefficient of initial uptake decreases slightly with the increase of relative humidity. It should be pointed out that the effective surface area of SiO<sub>2</sub> particles, which is represented as a BET area, is assumed to remain constant under different relative humidity in this study. However, the effective surface area of particles would change with the presence of water vapor [19-21]. Thus, it seems more accurate for determining  $y_0$  with the effective surface area of particles dependent on the corresponding relative humidity. But it is difficult to obtain such an effective surface area, due to the limitation of the measurement principle of the BET area. We hope the hydrated area can be characterized with the improvement of technique in the future. Even though this problem has not been solved, it is proposed that the presence of water vapor only has a slight influence on the  $\gamma$  value.

#### 2.4 Mechanisms of adsorption and desorption

As mentioned above, the adsorption process of acetone on the surfaces of SiO<sub>2</sub> particles is in a nonreactive and reversible state. The rates of initial adsorption and initial desorption as well as the coefficients of initial uptake change slightly with the presence of water vapor in air, as shown in Table 2. But water vapor in air can significantly influence the concentration of acetone adsorbed on SiO<sub>2</sub> particles at equilibrium as well as the concentration of acetone remaining on the surface during the desorption in air, as shown in Table 1. Unlike the case of dry air in which about half amount of acetone molecules is inclined to remain on SiO<sub>2</sub> particles, almost all of acetone molecules escape from SiO<sub>2</sub> particles in the humid air with 60% relative humidity. These results imply the mechanisms of adsorption and desorption.

The explanation of these results needs a knowledge about surface forces. In addition to the weak van der Waals (or dispersion) forces, which results in a physisorption, it is speculated that stronger forces may present on the surface of SiO<sub>2</sub>. From the analysis of T-FTIR spectra mentioned above, it is concluded that there are obvious surface hydroxyl groups and hydrogen bondings on the surfaces of SiO<sub>2</sub> particles in dry air. Thus we propose that a considerable amount of acetone molecules are absorbed on SiO<sub>2</sub> by the hydrogen bonding interaction between carbonyl groups and surface hy-

droxyl groups of SiO<sub>2</sub> particles as follows:

Surface hydroxyl groups provide a stronger force to adsorb acetone molecules than van der Waals forces do. An adsorption due to the hydrogen bonding interaction is usually called semi-chemisorption. Under the condition of dry air, a majority of the acetone molecules are adsorbed on SiO<sub>2</sub> by this force, thus acetone molecules are inclined to stay on the SiO2 surface during the desorption process. By contrast, the role of this force is less important in the case of humid air. From Figure 3, it can be seen that when the adsorption ran in humid air, the negative peak intensity of isolated hydroxyl groups at 3736 cm<sup>-1</sup> decreased. This means that the amount of isolated hydroxyl groups on SiO<sub>2</sub> particles for absorbing acetone molecules decreased, revealing that water molecules will consume or overlap isolated hydroxyl groups of SiO<sub>2</sub> surface. Moreover, new hydroxyl groups are not formed by the following reaction<sup>[22]</sup>:

$$\begin{array}{ccc} & & & OH & \cdots & OH \\ & | & | & | & \\ H_2O + -Si - O - Si - & \longrightarrow & -Si & Si - \end{array} \tag{5}$$

In summary, the total amount of isolated hydroxyl groups on the surface of SiO<sub>2</sub> particles decreases under the condition of humid air. This results in a decline of equilibrium adsorption ability of SiO<sub>2</sub> particles.

#### 3 Conclusions

Based on the investigation of heterogeneous processes of acetone on SiO<sub>2</sub> particles and the kinetics analysis under the simulated atmospheric conditions, the conclusion is drawn as follows: (1) Acetone molecules are nonreactively and reversibly adsorbed on the surfaces of SiO<sub>2</sub> particles by van der Waals forces and hydrogen bonding forces, and the latter play a more important role in the adsorption process. The presence of water vapor can affect the adsorption ability for acetone on SiO2 particles by consuming or overlapping the surface isolated hydroxyl groups. (2) For the reaction of acetone on SiO<sub>2</sub> particles, the rates of initial adsorption and initial desorption, initial uptake coefficients and adsorption concentrations at equilibrium have been determined at different relative humidities. It is found that the initial uptake coefficient would decrease slightly with the increase of relative humidity, but the equilibrium adsorption amount of acetone molecules would decrease significantly with the increase of relative humidity. (3) In the desorption process in the acetone-free air, a considerable amount of acetone molecules will remain on SiO<sub>2</sub> particles in dry air, whereas the acetone molecules almost completely escape from SiO<sub>2</sub> particles into the gas phase at a high relative humidity.

The significance of the heterogeneous reactions of acetone on  $SiO_2$  needs to be evaluated. Using a model based on the heterogeneous uptake coefficient  $\gamma$  and the loss rates by photolysis along with representative loss rates for reaction with OH and  $NO_3$  radicals using typical concentrations in the atmosphere, Li et al. suggested that the heterogeneous loss rate on  $SiO_2$  particles measured for acetone is comparable to that from gas phase

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processes in urban or dust conditions<sup>[5]</sup>. But this model used a  $\gamma$  value determined in the absence of air and water vapor under a low pressure, which is three orders of magnitude greater than the value determined by our study under the simulated atmospheric conditions. As mentioned above, the large  $\gamma$  gap between our result and the value from the literature mainly derives from the difference between the conditions used in these two determining methods. Thus it seems to be more appropriate to draw a conclusion about the heterogeneous fate of acetone in the atmosphere with a model based on the atmospheric condition. However, up to date, such a model has not been set up. A model fitting the atmospheric condition is expected to evaluate the role of heterogeneous reactions of acetone and other carbonyl compounds in the atmosphere.

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